

CHEMICAL ABSTRACTS

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I—APPARATUS

C. G. DERICK

A simple form of Kipp's apparatus for the generation of hydrogen sulfide. V. B. CONNELL. *Pharm. J.* 106, 17(1921).—Of 2 bottles of equal size, one is inverted above the other. Both are closed with 2-hole stoppers and suitably fitted with glass tubing. The lower bottle has a layer of asbestos on which rests the FeS. The bottle is partly filled with the dil. H_2SO_4 . When the outlet is closed, the gas generated forces the acid into the upper bottle, as in Kipp's app.; when the outlet is opened, the reverse flow takes place.

S. WALDBOTT

A slight modification in Victor Meyer's vapor density apparatus. T. S. PATTERSON. *Chem. News* 121, 307(1920).—The outer jacket of the app. consists of a Cu tube closed, by brazing, at the lower end and having a short side tube brazed on at the upper end. A small condenser is fitted into this side tube. The inner tube contains a small amt. of Hg to break the fall of the bulb, which is released as described in *C. A.* 2, 1217.

G. W. STRATTON

Note on the measurement of the density of minerals. L. H. ADAMS. *Geophys. Lab., Am. Mineral.* 6, 11-12(1921).—The marked advantages of a flat-top pycnometer for measuring ds. are pointed out, and brief details of manipulation given. The wt. of the app. filled with liquid can be detd. to within 0.1 mg., which implies an accuracy of about 0.0001 in the d. of an ordinary solid.

E. T. WHERRY

Reversible mercury manometer with dampened oscillations. PIERRE MENARD. *Compt. rend.* 171, 1129-30(1920).

DONALD W. MACARDLE

A new method of joining glass. C. O. FAIRCHILD. *J. Optical Soc. Am.* 4, 496-503(1920); cf. Parker & Dalladay, *Trans. Faraday Soc.* 12, 305.—This method is particularly applicable for joining lenses, making colorimeter tubes, plane glass incandescent bulbs, etc. The object is heated in a small electric furnace to approx. its annealing temp., sufficiently high to avoid cracking while applying heat locally, and the junction of the two parts is rapidly passed over with a small oxy-gas blowpipe flame. By this method complete fusion of the junction can be accomplished without propagating beyond a restricted portion near the joint the stresses occasioned by local heating; hence it is applicable where a slight deformation at the junction does not impair the usefulness of the object. The furnace can be quickly heated so that a small glass article can be raised to temps. above the annealing temp., the junction completed by application of the flame, and cooling initiated before the glass has had sufficient time to appreciably change its shape. The two parts need not be of the same glass, nor need there be a perfect fit; the method fails only for glasses which have too widely differing coefficients of thermal expansion.

DONALD W. MACARDLE

A simple method for the preparation of ultrafilters. E. KNAFFL-LENZ. *Vienna. Kolloid-Z.* 27, 315-6(1920).—A collodion sack is prepd. in a cryst. dish of the same size and shape as a suction funnel, and is then transferred to the funnel. Higher than 3% collodion soln. gives a membrane of uneven thickness. If water is added before all the ether has evapd. there is greater absorption and a more pervious membrane is formed than if the ether is entirely evapd. first.

H. I. MATTILL

A colorimeter operating on the subtractive principle. L. A. JONES. *J. Optical Soc. Am.* 4, 420-31(1920).—For field and com. use, a colorimeter utilizing the subtractive principle of color mixt. seems to combine best the features of portability, simplicity of operation, and freedom from the necessity of delicate adjustment of parts. An image of the object whose color is to be measured is brought by a lens system so that it occupies one half of the field of the colorimeter tube. A neutral gray filter can be used if necessary to control the intensity of the light from the object so that it shall fall within the range of the instrument. The standard of comparison is an incandescent bulb which, with the proper current supplied through a control box and a suitable filter, gives a light matching noon sunlight; this is checked occasionally against a standard light. Four gelatin wedges are so placed that they may be inserted to any extent or withdrawn completely from the path of the beam of light from this source to the field of the instrument. Three of the wedges are of the subtractive complementary colors: minus green (transmitting red and blue), minus blue (transmitting red and green), and minus red (transmitting green and blue); the fourth wedge is neutral gray to control the light intensity. By proper adjustment of these wedges any color can be matched; the position of each wedge is indicated by a pointer and can be read on a graduated scale. While the instrument was designed primarily for the measurement of the color of objects at some distance, it can be easily adapted to examine transparent colored solids, liquids, or reflecting surfaces. D. W. M.

Photoelectric photometer. ARTHUR H. COMPTON. *Trans. Illum. Eng. Soc.* 15, 28-33(1920).—Other elec. photometers, such as the Se cell and the thermopile or bolometer with suitable absorption screens, have not been found adaptable to industrial photometry. As compared with optical methods of photometry, the photoelec. photometer has all the advantages of a deflection instrument over one which requires the judgment of small differences of degree. It is obvious that an instrument of this kind cannot entirely replace the visual photometer, since the eye is the final authority in estg. illumination. But when the photoelec. photometer has been adjusted to make true measurements of intensity of illumination, it effects the advantages of greater speed, less fatigue and higher accuracy where a large number of measurements on similar lamps is to be made. C. advocates the use of a K hydride photoelec. cell containing He. Cs and Rb, though sensitive to somewhat longer wave lengths than is K, are less practicable commercially on account of their lower melting points. The photoelec. current is magnified with a 3-electrode valve and a screen is employed which transmits radiation longer than about 5300 Angstrom units. Expt. has shown that it is not difficult to compare the spherical candle power of two similar lamps to within a probable error of 0.1%. A diagram of elec. connections is shown. D. MACRAE

A new study of the leucoscope and its application to pyrometry. IRWIN G. PRIEST. *Bur. of Standards. J. Optical Soc. Am.* 4, 448-95(1920).—The leucoscope is an app. originally suggested by Helmholtz, in which, by polarization, the entering light is sepd. into 2 complementary parts, which can be made equal in their effect on the eye, and therefore of the same color as the original. For white light one complementary part will contain mainly yellow and blue, the other red, green, and violet. In practice the match is not perfect; one complementary is yellowish, the other bluish, but they can be made equally red. The necessary division of the light depends on the spectral sensitivity curve of the eye; when the character of the light changes, the setting of the instrument will have to be changed to make a match. The leucoscope can thus measure color temp. and can be used as an optical pyrometer which requires no auxiliary app., either elec., or a comparison source of light. Priest refers to an article by Koenig (*Ann. Physik.* 17, 990(1881)) for a description of the instrument; he reports a test of its efficiency. He finds that there is a difference in the readings of diff. observers, but the calibration curve detd. for any one does not change appreciably, not even

when the observer is feeling unwell; the av. agreement reached with an imperfect instrument is about 15° at 2000°K , and better at lower temps., though over 100° at 5000° . The instrument was further studied, as well as its application in finding the color temp. of light sources, illustrated by daylight.

W. P. WHITE

Distance-reading thermometer. ANON. *Engineering* 110, 736-7(1920).—An instrument of great accuracy constructed by Messrs. Negretti and Zambra of London. Errors due to temps. of the capillary connecting the bulb with the indicator are eliminated by making the capillary of material of high expansion and running throughout its length a wire of material of low expansion. The space not occupied by the wire contains the working liquid, and the vol. of the wire and liquid and the capacity of the tube are so calcd. that for a given change in temp. the change in vol. of the liquid is the same as the change in space it can occupy. The indicator is a Bourdon gage with all gears and levers eliminated, and having a bimetallic strip to compensate for variations in its temp. The error due to the height of the bulb with respect to the indicator is eliminated by a device for adjusting the zero.

G. W. STRATTON

Recent progress in the construction of hydraulic accumulators. OTTO SCHLENKER. Cannstatt. *Chem.-Ztg.* 44, 975-6(1920); 3 cuts.—Instead of the old type of app. in which the desired pressure is transmitted to hydraulic machines by means of a load placed on top of an inverted tank, like a gas holder, the pressure is more conveniently provided by means of compressed air in steel flasks.

J. H. MOORE

Separation of slimes from liquids by centrifuging. BERTHOLD BLOCK. Charlottenburg. *Chem. App.* 8, 3-5(1921); 3 cuts.—This is the 5th supplement to B.'s article (*C. A.* 14, 1872) in which he considers "the combination of the unperforated centrifugal drum with a filter."

J. H. MOORE

The technic of the filtering drum. LÉONCE FABRE. *Industrie & chimie* 7, 348-9 (1920).—A description of the construction and method of operation of the Zenith filter, and of the advantages which it presents in filtering slurries in the chem. industries (caustification of Na_2CO_3 , manuf. of NaHCO_3 , cement ind., etc.).

A. P. C.

Static notched-bar testing machine. ANON. *Chem. Met. Eng.* 23, 1180(1920).—If a notched bar specimen is broken slowly by static pressure the work expended is comparable to that measured by a dynamic impact machine, and is much more effective in distinguishing between brittle and ductile metals. J. C. W. Humphry's app. operating on this principle is described and illustrated. By its use a curve is obtained plotted in foot-pounds and radians as axes, and the total energy absorbed in breaking the test piece can be calcd. from the graph, or can be obtained automatically by an integrating device fitted to the machine.

W. C. EBAUGH

Normal or standardized fittings. ALFRED STOCK. *Z. angew. Chem.* 33, I, 280 (1920).—Could one replace the varied cuts or tapers on stopcocks, necks of vessels, etc., with normal or standard forms, making the parts interchangeable, it would mark an extraordinary advance in app. manuf. To be entirely successful such parts must be made so as to require no final grinding or fitting by the purchaser and user. Adapters and connections for extn. flasks and other app. are better when made of the insert, rather than the slip-over or cap type.

W. C. EBAUGH

Tests of carbon monoxide detector in mines. D. HARRINGTON AND B. W. DYER. Bur. of Mines, *Rept. of Investigations* No. 2207(1921).—A simple compact device has been developed for the rapid detection of small, though dangerous quantities of CO in mines. A sample of the air mixt. is drawn into a small rubber bulb, and forced through a glass tube filled with chemicals which change in color from gray or white to shades of green according to the CO content. A color scale is attached for comparison and detn. of CO percentages. Comparative data show results accurate for concns. of 0.1% and greater. A possible hazard in using the detector alone is color-blindness. The sources of light in mines vary widely, making detection difficult. Color changes

are made uncertain by variance in the dust, smoke and moisture content. Although dangerous to rely on a negative detector test, the production of a green coloration proves its presence, and its warning should be heeded. W. H. BOYNTON

Board for testing small electrochemical equipment (PLATT) 4. Hydrometer for small amounts of gasoline (ANDERSON, HINCKLEY) 22. The repair of crystallized glass apparatus (GERMANN) 19.

Acetylene generator. L. W. HAMILTON. U. S. 1,365,913, Jan. 18.

Acetylene generator. F. TURNER and T. BURTON. U. S. 1,365,570, Jan. 11.

Photochemical apparatus. W. O. SNELLING. U. S. 1,365,740, Jan. 18. Bell jars inverted over a liquid seal and exposed to actinic rays from an adjacent lamp are used as reaction chambers for gas reactions such as chlorination of hydrocarbon gases. Independently adjustable screens are arranged between the lamp and the reaction vessels.

Apparatus for filtering mineral oils or other liquids. J. P. WINTERS and M. McCAMON. U. S. 1,366,143, Jan. 18.

Gas burners for drying ladles. FRED W. ALLES, ALEX. FLETCHER and GEO. E. HITCHENS. Can. 208,902, Feb. 22, 1921. App. is specified for drying ladles by introducing therewith the flame from a fluid fuel burner.

Draft regulators. JAS. O. ANDERSON. Can. 208,636, Feb. 22, 1921. The app. comprises a water container, a flue having at its upper end a return bend which extends into the container and means for supplying water to the container to predet. elevations and with respect to the discharge end of the flue whereby the draft is regulated.

Separating mercury from amalgam. S. H. COCKS. Brit. 152,815, Aug. 9, 1919. App. for sepg. Hg from amalgam comprises a chamber provided with a screwed air-tight cap, a perforated base secured to the chamber by a clamp, a filtering-medium, such as canvas, overlying the base, and a valved pipe for introducing air or water under pressure.

Apparatus for making extracts. T. P. TUTT. U. S. 1,365,068, Jan. 11. The app. is especially adapted for prepg. ext. of coffee.

Apparatus for concentrating food or other solutions. E. E. HORSTMANN. U. S. 1,365,916, Jan. 18.

2—GENERAL AND PHYSICAL CHEMISTRY

W. E. HENDERSON

Friedrich Christian Accum (1769-1838). "AINOS." *Pharm. J.* 106, 15-7(1921).—An account of his life, with portrait, and review of his books on applied chemistry (1803-24). S. WALDBOTT

A hundred years of electromagnetism: Hans Christian Oersted (1777-1851). JERMSTAD. *Arch. Pharm. Chemi; Schweiz. Apoth.-Ztg.* 58, 660-1(1920).—A brief biography of Oersted, who began as an apothecary. S. WALDBOTT

A recurring error (history of mercury). CH. M. VAN DEVENTER. *Chem. Weekblad* 16, 386-7(1919).—v. D. takes issue with Jaeger's statement that even in the time of Dioscorides Hg was considered a constituent of the metals. The confusion has arisen from the rendering of the word *metallois* which signifies not metal but mine.

I. H. ADAMS

A substitute for Thoulet's solution. A. THIEL and L. STOLL. *Marburg. Ber.* 53, 2003(1920).—In the detn. of d. by the method of suspension, the aq. solns. most used are those of potassium mercuric iodide (Thoulet), and barium mercuric chloride

(Rohrbach). The authors propose the use of $\text{Pb}(\text{ClO}_4)_2$ in place of these. The soln. is prepd. by treating perchloric acid with Pb carbonate and warming. The satd. soln. at 15° contains about 78% of $\text{Pb}(\text{ClO}_4)_2$, and its d. can be found accurately to the third decimal place with a Westphal balance. The d., 2.6, is not such as to make this soln. a complete substitute for the others, yet it covers a wide range and is relatively cheap.

R. E. HALL

Convenient form of the periodic classification of the elements. C. R. NODDER. Cambridge. *Chem. News* 121, 269(1920).—The elements are placed on a double spiral with two sets of axes.

I. W. D. H.

Mendelyev's table, from the last published atomic weights in 1917. (Two possible new elements.) G. BOURGEREL. *Mon. sci.* 10, 241-2(1920).—Jandric (*Mon. sci.* 10, 169 and 193) believed that there existed two still undiscovered elements of at. wts. about 152 and 216. B. discovered in 1917 in certain rare minerals from an unnamed source, two new elements corresponding to these. The first forms a chloride which is decomposed by heat. This leads to a value of 150 for the at. wt. It also forms a cyanide compd., probably of the form $\text{K}_2\text{R}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. The value obtained for the at. wt. by the decompn. of this is about 152. The second element, which B. supposes to be eka-erbium, was obtained from a mineral having a density greater than 4. With it was associated some of the first element. A hydroxide is obtained from the mineral which is not attacked by concd. acids after calcining. It is attacked by fusion with KHSO_4 . After fusion it is sol. in water and NH_4OH gives a flocculent ppt. sol. in HCl , giving a yellow soln. It may be pptd. from this soln. by ammonium hydrosulfide and the ppt. gives a white oxide on calcining. The hydroxide gives up 29 to 29.5% water on calcining. On heating the oxide to 1000 – 1100° in H_2 it becomes gray and loses 3.4% of its wt. If the oxide were E_2O_3 this would give an at. wt. of 211. A form of the Mendelyev table is given.

E. H. DARBY

A new periodic relation between the atomic weights of the chemical elements.
II. The law of mirrored remainders. K. FEHLE. *Physik. Z.* 21, 382-5(1920); cf. *C. A.* 15, 195.—The differences between the exptly. obtained and the "ideal" at. wts. (cf. *C. A.* 14, 3174) of elements of at. numbers 37-74, are the mirror images of the corresponding members of the series of differences from at. numbers 1-37. F. has obtained this relation by plotting the differences as ordinates against the at. numbers as abscissas, making a mirror form for at. nos. 1-37, and laying this on the chart for at. nos. 37-74. The law is used to better uncertain at. wts., and to fill in blanks in the series. Thus he finds $\text{Ge} = 72.0$; $\text{Mo} = 98.1$; $\text{X} = 130.0$; $\text{Yb} = 171$. For the element of at. no. 43, he predicts 98.7; no. 61 = 146.3; $\text{Lu} = 175.0$; $\text{Ta} = 180.5$; $\text{W} = 183.5$; no. 72 = 177.7; no. 75 = 187.3. The significance of the law lies not in its relation to the periodic system of the elements, but in that it proves that irregularities in at. wts. are not irregularities of departure from whole numbers, but of the ideal at. wt. series.

R. E. HALL

The hypothesis of the unity of matter. C. DE MARIIGNAC. *J. chim. phys.* 18, 261-9(1920).—The idea that a few primitive elements make up matter is old, but they were formerly conceived to be properties, not indivisible matter as now. M. considers three properties of matter, weight (at. wt.), vol., and heat capacity. He shows that wt. is a sp. property of elementary matter, sp. heats and elec. properties depend on the grouping of elements and are thus essentially properties of the second order while vol. is a property of a still higher order. He concludes then, that the elements can never be decomposed, since heat and elec. energy for example, will only effect elementary groupings and not elements, and that the forces which impress upon elements their essential characteristics are greater than man can hope ever to overcome. Hence, the question of the fundamental unity of matter, while highly probable theoretically,

will always remain a purely theoretical question. No mention is made of modern electronics or radioactivity.

E. H. DARBY

Heat of sublimation of carbon. H. KOHN. Univ. Breslau. *Z. Physik* 3, 143-56 (1920).—K. shows that Fajan's calcn. of the heat of sublimation of C (*C. A.* 14, 1623) from the pressure-intensity relation of the C arc can be improved in the matter of temp. measurement. He assumes instead of $I = aT^x$ the better relation $\log I = -k/T + \text{const.}$ which has been experimentally tested. This gives for the Clausius-Clayperon equation $\log p = (\lambda/Rk) \log I + \text{const.}$, connecting λ , the heat of sublimation, directly with the intensity I . K. repeats the measurements of Lummer (Liquefaction of Carbon and the Production of the Sun's Temperature. Braunschweig 1914; cf. *C. A.* 9, 143) and shows the intensity is independent of energy input. With the temp. correction the value of λ for C is 163.5 kg. cal. (168 for diamond) where the measurements are from 0.3 to 8 atm. This is in better agreement than Fajan's value with the result 142 kg. cal. obtained from the integrated vapor pressure equation and Nernst's values for the chem. const. of monatomic gases.

F. C. HOYT

Heat of combustion and work of dissociation. I. A. v. WEINBERG. *Ber.* 53, 1347-53 (1920).—The validity of four laws regarding the heat of combustion of org. substances stated in a previous paper (*C. A.* 14, 1332) is discussed more fully. No new results are given. II. *Ibid* 1519-28.—The values of the heat of combustion for a great variety of at. groups common in org. compds. are calcd. Results from different sources check well. The following table gives the final results:

	H-H	(C) π	N \equiv N	O=O	S=S	Cl-Cl	Br-Br	I-I	
Q.....	81.3	177.6n	266.4	118.6	104.5	113	47	36.3	
Valence.....	2	4n	6	4	4	2	2	2	
Q/valence.....	40.6	44.4	44.4	29.6	26.1	56.5	23.5	18.1	
	H-C	H-N	H ₂ =O	H-O	H ₂ =S	H-Cl	H-Br	H-I	
Q.....	88.8	88.8	198.5	97.8	152.8	119.2	76.3	59.4	
Valence.....	2	2	4	2	4	2	2	2	
Q/Valence.....	44.4	44.4	49.6	48.9	38.2	59.6	38.2	29.7	
	C-C	C=C	C \equiv C	C-N	C=O	(CO)	(CO ₂)	C-S	
Q.....	88.8	148.6	202.6	77.1	88.5	265.5	392.2	73.1	
Valence.....	2	4	6	2	2	6	8	2	
Q/Valence.....	44.4	37.1	33.9	38.6	44.3	44.3	49.0	36.5	
	C-Cl	C-Br	C-I	(NO)	(NO ₂)	(SO ₂)	(SO ₃)	Cl-S	Cl-O
Q.....	119.5	74.2	54.5	170.9	243.7	254.5	336.2	71.2	78.8
Valence.....	2	2	2	5	7	6	8	2	2
Q/Valence.....	59.7	37.1	27.2	34.2	34.8	42.4	42.0	35.6	29.4

E. D. WILLIAMSON

Figures produced by the crystallization of potassium dichromate. MASAMICHI KIMURA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 4, 173-8 (1920).—A soln. of $K_2Cr_2O_7$ when evapd. on a glass plate gave 3 different crystal formations: (1) Some crystals grew from the boundary of the soln. toward the center. (2) Some grew coral-shaped on the outside boundary of the soln. (3) In the center seaweed-like forms appeared rapidly from supersatd. solns. When the soln. was poured on gelatin films only the 3rd forms resulted. K. explains this on the grounds that the gelatin absorbed the solvent and caused supersatn. The mols. and mol. aggregates were therefore unable to diffuse rapidly enough to form normal crystals as in 1. The mobility of the mols. was further reduced by adding gelatin to the soln. whereby the seaweed formation was much less regular. K. favors the view that the formation or dissolution of a crystal is detd. by the balance of elec. forces between the mols. of the solute and the solvent.

E. B. SPEAR

The crystal structure of calcium. A. W. HULL. *Gen. Elec. Co. Phys. Rev.* 17, 42-4 (1921).—The diffraction effects obtained by the "method of powders" indicate that the atoms of Ca have a face-centered arrangement. The length of the side of the unit cube is found to be 5.56 Å.

RALPH W. G. WYCKOFF

The crystal structure of ice. D. M. DENNISON. *Gen. Elec. Co. Phys. Rev.* 17, 20-2 (1921).—The diffraction effects obtained by the "method of powders" indicate that "the lattice of an ice crystal corresponds to a hexagonal close-packed arrangement of mols., consisting of 2 sets of interpenetrating triangular prisms with sides 4.52 Å. and height 7.32 Å."

RALPH W. G. WYCKOFF

The fundamental constants of nature. HAWKSWORTH COLLINS. *Chem. News* 122, 2-4 (1921).—Basing his argument on the formulas for mol. refractivity and magnetic rotation, and on his theory that the relative vols. of the elements reveal the constitution and structure of atoms in a definite manner, the author asserts that the relative vols. of the elements are the fundamental constants of nature. He shows that at any definite temp., the relative vol. of CH₂ for the paraffin series is exact. R. E. HALL

The angle of slope (Böschungswinkel)—a new physical constant. A. LANGHANS. *Kolloid-Z.* 27, 101-23 (1920).—This const. is defined as the angle (β) which the sloping side of a pile of discrete material forms with the horizontal. The original must be consulted for complete data on the 90 different salts, metallic powders, and org. compds. studied by L. Extensive tables give the value of β detd. by 3 methods in each case together with measurements of the av. size of the particles and their sp. wt. Values found in the literature for sand, clay, gravel, etc., are also tabulated, and the importance of this const. in relation to the handling of such substances is emphasized. App. and methods for the accurate detn. of β are given. L. discusses the theory involved, and the relationship of β to the sp. wt., size, and coeff. of friction of the particles.

H. W. BANKS, 3RD.

Pure propane; weight of the normal liter. JEAN TIMMERMANS. *J. chim. phys.* 18, 133-41 (1920).—The normal d. of C₃H₈ was detd. in accordance with the technic which has been developed by Ph. A. Guye. Details are given for the prepn. of C₃H₈ by the method of Lebeau (*Compt. rend.* 140, 1042, 1454), and of Stahrross (*J. chim. phys.* 10, 497), and for its purification. The mean wt. of the normal l. of C₃H₈ prepd. by Lebeau's method was 2.01986, and by Stahrross' method, 2.01987. The rounded value is 2.0200. From these data and Lebeau's values of the crit. consts. of C₃H₈ the at. wt. of C was calcd. by several methods. The results were high, 12.03 to 12.08. Therefore, before the at. wt. of C can be calcd. definitely from the author's results, it will be necessary to make more accurate detns. of the crit. consts., and of the coeff. of compressibility of C₃H₈.

R. H. LOMBARD

The boiling points and the critical temperatures and pressures in homologous series. MAURICE PRUD'HOMME. *J. chim. phys.* 18, 94-102 (1920).—A number of relationships have been established between the abs. b. p., T_b , the critical temp., T_c , and the critical pressure, P_c , of members of several homologous series. In each homologous series the ratio (T_b/T_c) always increases from one member to the following, and there is always one member of a series for which the value of this ratio is very nearly 0.66. For the paraffin series, the alkyl chlorides, and the olefins, the difference ($T_c - T_b$) increases from member to member. This leads to the relation, $(T_c - T_b)/(T_b/T_c) = K$, or $T_c = (T_b/2) + [(T_b^2/4) + (KT_b)]^{0.5}$. The values of K for the above 3 series are, resp., 244, 275, and 251. The difference between the values of T_c for consecutive members of the paraffin series is expressed by the formula, $\Delta = 210/(T_c^{0.0135T} \sqrt{T_c})$. In the case of the Me-benzenes, the alkyl alcs., and the alkyl formates and acetates, ($T_c - T_b$) decreases as one goes up in the series, hence the relation, $(T_b/T_c)(T_c - T_b) = K$, or $T_c = T_b^2/(T_b - K)$. By combining this equation with the Ramsay and Young

formula, $T_1/T_2 = K$, there results, $(T_c - T_1)/(T_c - T_2) = K$, where T_1 and T_2 are the b. ps. at 2 different pressures. This expression was found to be const. for isomeric alkyl esters. The value of P_c decreases from one member to the next higher in a homologous series, and it is sensibly the same for isomeric alkyl esters. The following relation holds in the case of the paraffin series, and for a series of Et esters of the fatty acids, namely, $(T_c - T_1)^{P^n} = K$. The values of n for these two series are, resp., 0.229 and 0.122. For the He group of elements, and for the halogen group, the relation, $[T_c/(T_c - T_1)]/(T_1/T_c) = K$, holds remarkably well, the value of K being 4.06. The term $T_c/(T_c - T_1)$ is also fairly const. in these series. This same relation is true for the following series: MeCl, -Br ($K = 4.16$); EtCl, -Br, -I ($K = 4.26$); and C_4H_9F , -Cl, -Br, -I ($K = 4.34$). In these series the value of the term $T_c/(T_c - T_1)$ is also very const. Consequently, the introduction of F, Cl, Br, or I in a hydrocarbon gives const. values for (T_1/T_c) and $T_c/(T_c - T_1)$ which are independent of the nature of the halogen. In the case of several members of these homologous series whose critical consts. have not been exptly. detd., the value of T_c or P_c was calcd. from certain of the above formulas.

R. H. LOMBARD

Relation between the absolute temperatures of fusion, and ebullition and the critical temperature. M. PRUD'HOMME. *J. chim. phys.* 18, 307-10(1920).—The following relations between the b. p. (T_b), f. p. (T_f) and crit. temp. (T_c) hold: $T_f/T_c = K'_1$, $T_c/(T_c - T_f) = K'_2$, $[T_c/(T_c - T_f)] \cdot (T_c/T_f) = K'_3$. Values for K'_1 , K'_2 , and K'_3 are tabulated for 50 elements and compds. and for 3 metals, Fe, Cu and Au. The functions $T_c^2/[T_b(T_c - T_b)]$ and $T_c^2/[T_f(T_c - T_f)]$ appear to be characteristic functions of the elements and compds. They do not have the same values but are substantially const. for groups of similar compds. and elements. The general relation is: $T_f[T_c - T_f] = rT_b[T_c - T_b]$ where r varies between 1 and 1.1. For $r = 1$, $T_c = T_b + T_f$. This is exactly true for H_2O , PH_3 , CH_3Br , C_4H_9Cl and $CO(CH_3)_2$.

E. H. DARBY

Some relations between the absolute critical temperature and the absolute boiling point. M. PRUD'HOMME. *J. chim. phys.* 18, 270-2(1920).—Three relations exist connecting b. ps. [T_b] and the crit. temp. (T_c). (1) $T_b/T_c = K_1$; (2) $T_c/(T_c - T_b) = K_2$; (3) $[T_c/(T_c - T_b)] \cdot (T_c/T_b) = K_3$. Values of K_1 , K_2 , and K_3 are tabulated for 49 elements and compds. Going up in a homologous series [T_b/T_c] increases, and [$T_c - T_b$] may increase or decrease continuously throughout the entire series. For the first case: $[T_c - T_b](T_c/T_b) = C^{te}$ and for the second: $[T_c - T_b](T_b/T_c) = C^{te}$. Formula I applies to the following series: paraffins, chloroparaffins, olefins, ethers, amines, nitriles. Formula II applies to: methylbenzenes, other substituted benzenes, esters, bromoparaffins, iodoparaffins and phenols.

E. H. DARBY

The thickness of the layer of liquid adhering to the wall of a vessel. JULIUS MEYER. Breslau. *Z. physik. Chem.* 96, 275-86(1920).—Detns. have been made of the thickness of layers of the liquid adhering to the surface of Cu in contact with H_2O . When the thermal conc. of the liquid is known, the thickness of the adhering layer may, under certain conditions, be calcd. from the quantity of heat transmitted through the metal by means of the following formula: $d = \lambda t f [T_1 - (T + T')/2] / 2g(T' - T)$. Here g is the quantity of liquid contained in a spherical metal vessel immersed in a bath of the same liquid; d is the thickness of the layer of liquid adhering to either side of the metal; λ is the thermal cond. of the liquid; f is the area of the metal surface; T_1 is the temp. of the bath; T is the initial temp. of the liquid in the vessel and T' is its temp. at the end of t secs. From expts. carried out with H_2O and Cu the value 0.006-0.009 mm. has been calcd. for the thickness of the layer of H_2O adhering to the Cu. From the expts. of Grätz on the passage of liquids through tubes (cf. *Wied. Ann.* 18, 79; 25, 337) values between 0.0018 and 0.0043 cm. have been obtained for the

thickness of the liquid layer adhering to the side of the tube. The thickness of this layer is smaller the greater the velocity with which the liquid flows through the tube.

H. JERMAIN CRIGHTON

The swelling of gelatin in acids. W. R. ATKIN. *J. Soc. Leather Trades' Chem.* 4, 248-56, 268-71 (1920).—Exptl. results given by Procter (*C. A.* 5, 2491; 9, 875), Procter and Wilson (*C. A.* 10, 1807), Lloyd (*C. A.* 14, 1919), Fischer (*C. A.* 12, 590), and Loeb (*C. A.* 11, 2907; 12, 1973-4-5; 13, 326-7, 848, 1597) all show, when carefully studied, that the point of max. swelling of gelatin occurs at a H-ion concn. of 0.004 *N* in the external soln. or of 0.001 *N* in the jelly phase, whatever acids are used. It is shown that the quantity *e*, described by the Procter-Wilson theory as the excess of concn. of diffusible ions of the jelly over that of the external soln. and considered proportional to the swelling, also has its point of max. at a H-ion concn. of 0.004 *N* for a theoretical external soln. Additional evidence is thus furnished of the soundness of the Procter-Wilson theory.

J. A. WILSON

Tyndall phenomenon in liquids—according to the experiments of P. Wolski. M. LEBLANC. *Ber. Verh. Sachs. Akad. Wiss. Leipzig* 72, 24-7 (1920).—Using an ultrafilter consisting of a piece of taffeta silk treated with a one % alc. collodion soln., L. has obtained water, solns. of inorg. salts, acids, and bases, as well as a concd. soln. of an org. substance like citric acid—about 100 g. in 100 cc.—saccharin and sugar optically empty when observed with a Zeiss "Spalt" ultramicroscope. The Tyndall effect in the case of ordinary solns. is to be attributed to the presence of dust particles in the liquid and not to the action of mols. or mol. complexes.

D. MACRAE

Forces in surface films. A. M. WILLIAMS. *Proc. Roy. Soc. (London)* 98A, 223-34 (1920).—(I) *Theoretical considerations.* Considering the detn. of *d* of a finely divided solid by the immersion method (assuming complete removal of air, etc.), let each g. of solid have a surface film weighing α g., whose mean sp. vol. is v_2 instead of v_1 , the value for the liquid in bulk. If v is the true sp. vol. of the solid, and v_0 that taken without considering α , then $v = v_0 + \alpha(v_1 - v_2)$, where the last term becomes important only with large development of sp. surface, and because of varying compressibilities varies from liquid to liquid. Since the adsorbing surface is more accessible to smaller mols., in the case of any other liquid than the standard, water, a correction Δv must be added to v , Δ being the fraction of the surface inaccessible to the liquid being used. If p = the pressure which changes v_1 to v_2 and β = the mean compressibility of the liquid within this range, then $v_1 - v_2 = p\alpha\beta$; whence $v + \Delta v = v_0 + \alpha p\beta$. This compressive force is approx. equal to the cohesive force in liquids, represented by a/v^2 in van der Waal's equation. Assuming plane surface contact (which will give smaller values for pressure than capillary contact) $p + a/v^2 = A_0^{1/2}/v \times A^{1/2}/v_2$, where A_0 and v refer to the solid and a and v_2 refer to the liquid. "Since observations on the compression of a liquid give us the relation between p and v_2 , if we det. one of these we can further det. A_0/v^2 or the "internal" pressure of the adsorbent. (II) *Experimental observations and calculations.* Highly purified blood charcoal showed a v_0 with water of 0.511 and with CH_2Cl of 0.461, using a sp. gr. bottle similar to that described by Cude and Hulett (cf. *C. A.* 14, 1073). The values of α for H_2O and CH_2Cl were detd. by observing the mass of vapor picked up at 25° by 1 g. of evacuated charcoal from the satd. vapor; they were 0.75 for H_2O and 0.85 for CH_2Cl . These values for v_0 and α indicate that the cohesive force of H_2O at atm. pressure and 25° = 17,300 kg. per cm^2 ; CH_2Cl_2 = 2300 kg. per cm^2 ; the internal cohesion of charcoal 58,000 kg. per cm^2 . (III) *The charge on colloids.* Pressure causes an increased concn. of ions in the adsorption layer, which with C in contact with H_2O , figures out 0.034 volt lower than the surrounding fluid, which agrees with observations. "We therefore see that the existence in the adsorption layer of compressive forces of the magnitude given is sufficient to explain in sign and magnitude the potential differences

and apparent charge on certain particles suspended in fluids...we should expect that substances with a cohesion larger than water would appear negatively charged when immersed in it, while those with a smaller cohesive would appear positively charged. The positive ion of water moves faster than the negative ion, and we should have the reverse order of apparent charge in a fluid giving rise to ions where the negative ion moves faster than the positive ion." Chem. changes by giving rise to new ions even in traces may reverse the expected charge; *i. e.*, CH_2Cl dispersed in H_2O is negative because of formation of HCl . When negative As_2S_3 colloid is pptd. by BaCl_2 , the acidity of the supernatant liquid indicates that Ba^{++} is adsorbed preferentially, leaving outside the adsorption layer enough H^+ -ions to neutralize the effect of those in the adsorption layer, thus reducing or destroying the p. d. with consequent pptn. of the colloid.

JEROME ALEXANDER

Limiting size of colloidal particles in a Brownian motion. BUNSAKU ARAKATSU AND MITSU HARU FUKUDA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 4, 179-82(1920).—The diams. of the smallest particles that did not exhibit the Brownian movement in a colloidal soln. were measured by means of a cardioid ultramicroscope fitted with an ocular micrometer scale. Solns. of 11 different metals were employed. The value obtained for Au was 2.7μ . The average value for W, Au, Pt, Ag, Cu, Al, Ni, and Hg was 2.6μ . The relation of the viscosity of the soln. to these values was investigated by the addition of sugar and glycerol. It was found in the case of Au and Cu solns. that $\log_{10} \alpha$ plotted against $\log_{10} \eta$ gave a straight line, or that for Au, $\alpha \eta^{0.229} = 3.5$, and for Cu, $\alpha \eta^{0.249} = 3.4$, where α is the diam. of the particles expressed in μ and η is the viscosity of the soln. with water taken as unity.

E. B. SPEAR

Optically clear fluids. P. WOLSKI. *Kolloidchem. Beihefte* 13, 137-64(1920).—The fluids were examined by the Siedentopf-Zsigmondy slit ultramicroscope, the vol. illuminated being 0.00065 cu. mm. Ultramicros were counted with the fluid still (static method) and with the fluid flowing slowly (kinetic method). The number of ultramicros per cc. were: tap water, 2,000 to 5,000; ordinary distd. water, 80-150; cond. water about 90, which were however less bright than those in distd. water. As the distance between the ultramicros is about 0.2 mm. (10^7 times greater than the av. mol.), the turbidity was obviously due to dust particles. These can be removed by cataphoresis, but best by ultrafiltration through silk or linen filters impregnated with collodion, and thus were produced optically clear water and aq. solns. of inorg. salts, as well as various org. substances (alc., chloroform, benzene, etc.). The inhomogeneity of hydrolyzable salts (FeCl_3 , AlCl_3 , CaCl_2) is removed by a trace of acid. Ultrafiltration removed the inhomogeneity even from satd. solns. of citric acid, saccharin and raw sugar. It is concluded that the inhomogeneity previously reported in sugar, etc., is due to foreign substances.

JEROME ALEXANDER

Water-soluble colloids from artificial carbons. K. A. HOFMANN AND WILHELM FREYER. *Ber.* 53, 2078-95(1920).—The authors excluded from their investigation the almost white suspensoid obtainable from diamond dust, and used instead the dark colloid which is obtained as the first oxidation product under the most diverse conditions. Comprehensive expts. showed that the chem. structure of the original materials did not cause variations in the product, but rather the temp. at which the lampblack emerges from the gaseous intermediate products. In the following investigation, lampblack prepd. at a low temp. from petroleum, paraffin, ethylene and acetylene flames, burning benzene or naphthalene vapors, and charcoal made from pine wood, were used. The simplest and surest method of prep. usable colloids and obtaining good yield, consists in oxidation by K or Na chlorate in dil. HCl . The compn. of the colloids from lampblack which are insol. in H_2O , but sol. in very dil. alkali or 1% NaHCO_3 is $(\text{C}_7\text{H}_6\text{O}_2)_n$. The water-sol. colloid has the compn. $\text{C}_{11}\text{H}_4\text{O}_4$. The authors assume that the C atoms are at least partially of cyclic arrangement, this following from the

resistance of the colloids to oxidation. All are acid in character, especially the more highly oxidized water-sol. colloids. The colloid from wood charcoal, insol. in water, has the compn. $C_{10}O_7H_7$; sol. in water, $C_{11}H_7O_8$. Its characteristics are much the same as those of the others, though its color is more of a brown. The authors find the color intensity of the black carbons the same in order of magnitude as that of the higher mol. pigments. The dimensions of the alkali-sol. particles are $3-4 \times 10^{-8}$ cm.; of the water-sol., are $1.7-2 \times 10^{-6}$ cm. These are comparable to the particles in the red gold hydrosol of Siedentopf, which are 2×10^{-8} cm. The particles are charged electronegatively; apart from the salts and hydroxides of the alk. earths, various electrolytes will ppt. them. The particles from wood charcoal are least readily pptd.; the water-insol. particles of the lampblack are next in order, and lastly come the water-sol. particles. The cond. of dil. NaOH is very considerably lessened by these colloids. They rank very near to the best pulverized, insol. carbons in their power of adsorption. They change the surface tension of the solvent far less than gum arabic, dextrin, gelatin, fatty acids, etc., and are rather ultramicroscopic suspensions than emulsions. R. E. HALL.

The physics and chemistry of colloids and their bearing on industrial questions. Some observations on peptization and precipitation. N. G. CHATTERJI AND N. R. DHAR. *Chem. News* 121, 253-6 (1920).—AgCl, Ag_2CrO_4 , and calcium silicate are not peptized in the presence of concd. soln. of cane sugar (contrary to Bancroft—2nd Annual of Brit. Assn. on Colloid Chem.). Hydroxides of Fe, Ni, Th, Hg, Co, etc., were peptized by adding NaOH to solns. of the respective salts in presence of glycerol or sugar (in the case of V and Au, NH_4OH should replace NaOH). But glycerol and sugar will not peptize the hydroxides if added subsequent to pptn. It is a curious fact that prompt pptn. occurs if the salt soln. be added to a mixture of glycerol and the alkali hydroxide. No peptization seems to occur with $Sb(OH)_3$, CuF_2 , or $BaSO_4$. The cond. of a soln. of NaOH is not appreciably changed by the addition of the hydroxides of Cr, Al, Pb, Hg, but in the case of Zn the resistance increased appreciably. "Hence we can conclude that the solns. of $Al(OH)_3$, $Cr(OH)_3$, $Pb(OH)_2$, $Hg(OH)_2$, and $Cu(OH)_2$ are cases of true peptization and not of chem. combination. On the other hand, in the case of $Zn(OH)_2$, we get more of the chem. combination than of peptization." Confirming the work of Bentley and Rose (*C. A.* 7, 3882) freshly pptd. $Al(OH)_3$ is peptized by acetic acid; so also are $Fe(OH)_3$ and $Cr(OH)_3$. But with $Zn(OH)_2$ the cond. rises greatly, indicating that this more strongly basic hydroxide has mainly formed Zn acetate. Blue $Cu(OH)_2$ containing a trace of undecomposed Cu salt is stabilized by it, and does not turn black on boiling as would otherwise be the case. The protective adsorbed Cu salt may be washed out by hot water, and the black $Cu(OH)_2$ may be rendered blue on boiling with a trace of Cu salt. In general the stronger the kind of alkali, the more rapid was the change from blue to black— $KOH > NaOH > Ba(OH)_2$, etc. The color change of $Co(OH)_2$ from blue to pink is analogous to that of $Cu(OH)_2$ and is similarly effected by catalysts. "All those salts which produce a hydroxide sol. in excess of NaOH, namely, salts of Zn, Al, Sn, Pb, etc., markedly retard the transformation of both the blue $Cu(OH)_2$ to the black form, as well as that of the blue variety of $Co(OH)_2$ to the pink form. It seems probable that the presence of $Al(OH)_3$, $Pb(OH)_2$, $Sn(OH)_2$, etc., in the colloidal state tends to peptize the $Co(OH)_2$ or the $Cu(OH)_2$." $Fe(OH)_3$ when pptd. in solns. of the hydroxides of Al, Cr, and Zn in NaOH, adsorbs and carries down some of the latter hydroxides.

JEROME ALEXANDER

The balloelectric behavior of amphoteric substances. C. CHRISTIANSEN AND JOHANNES CHRISTIANSEN. *Danske Videnskabernes Selskab. Math.-fys. Meddelelser*. [II] 6, 35 pp. (1919); cf. *C. A.* 14, 2290.—C. found that aq. solns. of electrolytes mixed with nonconducting liquids, e. g., EtOH, become strongly balloelectric. (The ballometer is an instrument devised by C. for measuring the elec. charges conveyed by an

atomized spray upon a metal plate connected to a quadrant electrometer.) In this study amphoters like white of egg, serum albumin and Witte-peptone were used. Curves (ballograms) were drawn for each showing the effect of adding HCl, Na^+ , NaCl, H_2SO_4 , AcOH, etc. The curve for serum albumin is typical. Without acid and with small amounts of HCl it is +, drops rapidly below the zero line, rises again to positive and goes on indefinitely with increasing HCl. Higher concn. of albumin had no serious influence on the curve. From the start the swinging from + to - and back again was that to be associated with the isoelec. point of the amphoter, but there was no sharp coincidence between the isoelec. point and the zero balloelec. point in the serum curves. White of egg gave curves very similar to the above except that high concn. of albumin shows no part of the curve. The following substances were also examined: glycine, alanine, β -alanine, α -aminobutyric acid, aminoisobutyric acid, β -aminovaleric acid, leucine, norleucine and phenylalanine. The conclusion from the bulk of the work is that the isoelec. point of certain ampholytes is balloelectrically neutral while for others the point does not appear on the curves. Since serum and albumin show this point in a distinct manner and as Paulis has shown that the ions of these materials are strongly hydrolyzed it is reasonable to conclude that it is the hydrolyzation of their ions that makes them balloelectrically active.

P. M. GLASOE

The length of time of the color change of Congo rubin under the influence of electrolytes and protective colloids. HEINRICH LÜERS. *Kolloid-Z.* 27, 123-36(1920).—A study of the factors influencing the time taken by Congo rubin to change from red to blue. The time in sec. was measured from the time of addition of the electrolyte, protective colloid, etc., until the Congo rubin sol (0.01%) matched in color a blue-violet standard of the same substance. For example, in our series of expts., the following concns. of electrolyte were needed to bring about the change in 30 sec.: KCl, 100 millimols. per l.; MgCl_2 , 1.7 millimols. per l.; CeCl_3 , 0.54 millimols. per l. The results are not in exact agreement with the Whetham-Robertson valence rule. The Congo rubin sol follows closely the rules given by Zsigmondy for the coagulation of gold sol and the change of color from red to blue is for that reason considered to be a process of coagulation. At a given concn. of electrolyte the time is inversely proportional to the Congo rubin concn.; it increases with increasing viscosity of the soln. These facts support the theory developed, for coagulation is a function of the velocity of diffusion of the discharged particles. Gelatin was used in studying the effect of protective action on the time of the color change. The presence of gelatin lengthens the time of the reaction, and at a given concn. of electrolyte increase of concn. of gelatin increases the time. Changes in state of the gelatin itself (such as aging, effect of anions, tannic acid, etc.) influence greatly this protective action. These facts support the theory that protective action is due to a covering over of the particles by the protective substance (Umhüllungstheorie). All the results obtained point to the fact that the change of color studied is "a typical colloid phenomenon."

H. W. BANKS, 3RD

The solubility of copper hydroxide in strong sodium hydroxide solutions. E. MÜLLER. *Z. angew. Chem.* 33, I, 303-5(1920).—Copper hydroxide dissolves in concd. NaOH soln. (12 N) giving a violet soln. This gives a brown ppt. on standing that redissolves on the addition of more NaOH, giving a brown soln. M. discards the colloidal explanation and, after describing considerable exptl. work, arrives at the conclusion that the phenomenon is one of complex formation, thus: $\text{Cu}(\text{OH})_2 + 2\text{OH}^- = \text{CuO}_2^{2-} + 2\text{H}_2\text{O}$. Hence: $K = (C_{\text{OH}}^2/C_{\text{CuO}_2^{2-}})$ or, since the concn. of Cu is proportional to CuO_2 and that of NaOH to OH, he writes: $K = C_{\text{NaOH}}^2/C_{\text{Cu}}$. He determines these concns., and finds K is approx. const. between concns. of 6.09 and 15.50 mols. NaOH/liter.

E. H. DARBY

Dissociation of acid salts of dibasic acids in water. V. TH. SABALITSCHKA. *Ber.* 53, 1383-7(1920); cf. *C. A.* 14, 1539.—Solns. of the acid K salts of malonic, succinic,

maleic and fumaric acids were shaken with ether (McCoy's method, *C. A.* 2, 2036). Comparative expts. with maleic and fumaric acids show the dependence on the degree of dissoc. of the ratio of the two dissoc. consts. In the usual method of calcg. the second dissoc. const. the influence of the base is neglected, a proceeding on which S.'s results throw doubt.

F. D. WILLIAMSON

Molecular attraction. V. K. K. JÄRVINEN. Helsingfors. *Z. physik. Chem.* 96, 367-74 (1920); cf. *C. A.* 14, 1914.—It is shown that the mol. heat of vaporization of Hg at different temps., when calcd. with the help of the attraction law $F = m^2k/r^*$, is in better agreement with observed values when the exponent $n = 5.5$ than when $n = 5$ as previously given. It is further shown that values for the satn. pressure, p , calcd. from the mol. heat of vaporization obtained with $n = 5.5$ are in good agreement with observed data. In conclusion, an attempt has been made to calc. the heat of fusion of Hg, Pb, K, Na, Sn and Bi from the change in vol. during the passage from the liquid to the solid state. However, except for K and Na, the difference between the calcd. and observed values is large. It is pointed out that the exptl. data are very inexact.

H. JERMAIN CREIGHTON

The splitting off of halogen from some organic compounds. ARVID HJ. HEDBELLUS. Stockholm. *Z. physik. Chem.* 96, 343-66 (1920).—The equil. consts. in aq. soln. have been detd. for the reaction between NaOH and a number of organic halogen compds., the following values being obtained: $K_{CH_3ClCO_2H \cdot 10^3} = 2.05$ at 55°, 6.08 at 65°, 23.9 at 80° and 61.8 at 90°; $K_{CH_3BrCO_2H \cdot 10^3} = 151.0$ at 65°, and 365 at 75°; $K_{C_2H_5Br \cdot 10^3} = 113$ at 30° and 649 at 45° for the 1st step, and 2.8 at 75° for the 2nd. step; $K_{\alpha\text{-}CH_2Cl \cdot CO_2CH_3 \cdot CO_2C_2H_5 \cdot 10^3} =$ about 800. These values give for the const. A in the Arrhenius-van't Hoff temp. formula: $A_{CH_3ClCO_2H} = 23,000$, $A_{CH_3BrCO_2H} = 20,600$ and $A_{C_2H_5Br} = 22,000$ (1st step). The reaction between $\alpha\text{-}C_2H_5BrCO_2H$ and NaOH both in aq. soln. and in alc.-H₂O mixts. has been studied, but it has not been possible to det. the equil. const. owing to several simultaneous reactions taking place (cf. Senter and Wood, *C. A.* 10, 2581). While a velocity const. has not been obtained for the reaction between $NaOC_2H_5$ and CH_3COCH_2Cl , the course of the reaction is shown graphically. For several of the compds. the influence of EtOH, H₂O and CH_3COCH_3 on the reaction velocity has been studied.

H. JERMAIN CREIGHTON

Binary equilibrium system with solid carbon dioxide. A. THIEL AND F. SCHULTE. Univ. Marburg. *Z. physik. Chem.* 96, 312-42 (1920); cf. *C. A.* 8, 1229.—The previous investigation has been extended for the purpose of detg. more accurately the influence of the hydrostatic pressure of the liquid column on the equil. temp. of cold baths of mixts. of solid CO₂ with liquids. Temp. measurements have been made with the vapor pressure thermometer previously employed. The equil. has been studied of binary mixts. of solid CO₂ with the following liquid components: Et₂O, EtCl, SO₂, Me₂O, Cl₂ and H₂S at a pressure of 750 mm. The "Eigentemperature" (t_e), i. e., that temp. at which the vapor pressure of the liquid satd. with solid CO₂ is equal to the external pressure, of the above-mentioned systems has been measured. The deviation (Δt) of this temp. from that (t) of the pure CO₂-snow, representing the influence of the hydrostatic pressure of the liquid, is very small. For the systems CO₂-Et₂O, CO₂-EtCl, CO₂-SO₂, CO₂-Me₂O, CO₂-Cl₂ and CO₂-H₂S, this deviation ($t_e - t = -\Delta t$) is, resp., -0.008°, -0.022°, -0.033°, -0.172°, -0.83°, -3.50°. It has been found that the relation between the compn. of the vapor phase and t_e is in accord with the assumption that the solid phase is pure CO₂. Analyses have been made of both the gaseous and liquid phases of the system CO₂-Et₂O at several temps. between +15.2 and -78.6°, and the soly. of solid CO₂ in Et₂O has been detd. at -83.5°, -92.5 and -98.0°. From the data obtained the $t-x$ diagram has been constructed. This agrees with that of Roozeboom. The mol. % of CO₂ at equil. in the vapor phase of

the systems formed by solid CO_2 with Et_2O , EtCl , SO_2 , Me_2O , Cl_4 and H_2S is resp., 99.935, 99.70, 99.72, 98.65, 93.2 and 75.3, and in the liquid phase, resp., 47.4, 32.2, 33.6, 60.2, 17.5 and 25.4.

H. JERMAIN CREIGHTON

Thermodynamics of mixtures. IV. MARIO BASTO WAGNER. Lisbon. *Z. physik. Chem.* 96, 287-311(1920); cf. *C. A.* 14, 2440, 2880.—A mathematical paper. It is shown that Nernst's 2nd fundamental assumption for his heat theorem: "the decrease in the sp. heat of a given mass of gas takes place so much sooner the greater its density," follows from his 1st fundamental assumption: "every gas that is cooled at const. vol., condensation being excepted, assumes finally a condition of vanishingly small thermal capacity." Through consideration of a series of cyclic processes it is shown (1) that, for the same temps., in the region of solidification the thermal capacity of a gas at const. pressure, and therefore also its sp. heat, is greater the smaller the pressure under which the gas exists; (2) that a relation holds for the equil., vapor-liquid or vapor-solid, which is analogous to Planck's liquid-solid or solid-solid equil. formula. Three mathematical methods for the detn. of the vapor pressure of solids are developed. It is shown that the temp. of solidification of an ideal phys. mixt. can be calcd. from the f. p., T_1 and T_2 , of the components, according to the rule of mixts., provided (1) the 2 components are chemically very closely related; (2) the f. ps. of the components are close together; (3) the heats of fusion of the 2 substances are const.; (4) the heats of fusion are proportionately small, and (5) the heats of fusion have approx. the same value.

H. JERMAIN CREIGHTON

Deduction of the dissociation-equilibrium from the theory of quanta and a calculation of the chemical constant based on this. P. EHRENFEST AND V. TRKAL. *Proc. Acad. Sci. Amsterdam* 23, 162-83(1920).—Sackur (*C. A.* 7, 569) and Stern (*C. A.* 7, 3263) have attempted to derive relations for the "chem. consts.," C , by means of statistical mechanics and the quantum theory. E. and T. regard these derivations as not sufficiently rigid. According to their view, the numerical value of the chemical constant of a molecule should depend not only on its mass and moment of inertia, but also on the "symmetry number" of the molecule. The last corresponds to the number of completely equivalent rotational orientations. (Thus for I_2 it has the value 2, for CH_4 , 12.) The entropy calculated on the basis of statistical mechanical consideration is compared with that derived by thermodynamical methods and equations are thus obtained for the chemical consts. of monatomic, diatomic and poly-atomic molecules. These are practically identical with those derived by Sackur. S. D.

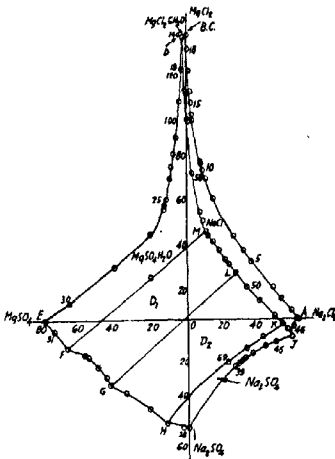
The solubility of acrolein in water, and of water in acrolein, at various temperatures. A. BOUTARIC. Collège de France, Paris. *J. chim. phys.* 18, 126-32(1920).—These solubilities were detd. by observing the temp. of the appearance, and the subsequent disappearance of turbidity in homogeneous mixtures of acrolein and H_2O of known compn. In satd. solns. rich in acrolein, the parts of H_2O per 100 parts of soln. increase from 3.98 at -8° to 13.25 at 53° ; and for satd. solns. rich in H_2O , the parts of H_2O per 100 parts of soln. decrease from 79.36 at 0° to 76.16 at 53° . Therefore, the concn. of H_2O in solns. of H_2O in acrolein, and the concn. of acrolein in solns. of acrolein in H_2O increase with the temp. These two soly. curves tend to meet at a critical temp. of soly., but the exptl. method did not permit the detn. of this temp. The effect upon these soly. relations of dissolving a third substance in the acrolein was studied. Acrolein which contains 1% of dissolved hydroquinone is less soluble in H_2O than is pure acrolein, which fact is in accord with Nernst (*Z. phys. Chem.* 8, 16(1891)). On the other hand, the soly. of H_2O in acrolein which contains 1% or 5% of hydroquinone, or 1% of gallic acid, is greater than in pure acrolein. It seems probable that these relations are general, namely: *The presence of a substance dissolved in a liquid, A, increases the soly. of another liquid, B, in the liquid A; and (Nernst) decreases the soly. of the liquid A, in another liquid B.*

R. H. LOMBARD

Thermochemistry of carbon linkages. A. THIEL. *Ber.* 53, 1378-82 (1920).—A reply to criticism by Fajans (*C. A.* 14, 3086). E. D. WILLIAMSON

Vapor composition of alcohol-water mixtures. P. N. EVANS. *Purdue Univ. J. Ind. Eng. Chem.* 13, 168-9 (1921).—D. defends his results on this subject (*C. A.* 10, 1002) which are considered unreliable by W. K. Lewis (*C. A.* 14, 1916). G. W. STRATTON

Equilibrium of the system water and the chlorides and sulfates of sodium and magnesium at 105°. TSUTOMU MAYEDA. *J. Chem. Ind. (Japan)* 23, 573-83 (1920).—In connection with salt manuf. from sea water M. studied this equil. The results are given in the fig. ($D_1 = 2\text{Na}_2\text{SO}_4 \cdot 2\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$, $D_2 = 3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$). The data related to the principle points are as follows:



	NaCl.	Na ₂ SO ₄ .	MgCl ₂ .	MgSO ₄ .	Solid phases.
A.....	60.72	NaCl
B.....	Trace	139.5	NaCl
C.....	139.5	NaCl, MgCl ₂ ·6H ₂ O
D.....	138.5	1.5	MgCl ₂ ·6H ₂ O, MgSO ₄ ·H ₂ O
E.....	123.1	2.020	MgSO ₄ ·H ₂ O
F*.....	76.60	MgSO ₄ ·H ₂ O
G*.....	13.07	64.31	MgSO ₄ ·H ₂ O, D ₁
H*.....	32.22	41.84	D ₁ , D ₂
I*.....	49.88	11.05	D ₂ , Na ₂ SO ₄
J.....	52.99	Na ₂ SO ₄
K.....	57.96	8.054	Na ₂ SO ₄ , NaCl
L.....	52.78	7.382	4.632	NaCl, Na ₂ SO ₄ , D ₁
M.....	27.02	10.12	33.64	NaCl, D ₂ , D ₁
	9.978	11.32	55.40	NaCl, D ₁ , MgSO ₄ ·H ₂ O

(The figures with an asterisk were obtained at 103°, and belong to the system H₂O-Na₂SO₄-MgSO₄.) S. T.

The theory of vapors. E. WERTHEIMER. *Ber. physik. Ges.* 21, 435-53 (1919).—A mathematical discussion of the equation of state of vapors together with a comparison of the pressure-vol.-temp. function for vapors with the radiation pressure-vol.-temp. relation for radiant energy. L. H. ADAMS

Some theoretical and empirical expressions with reference to surface tension, molar pressure, heat of evaporation, vapor pressure, and density, of coexisting phases. J. J. VAN LAAR. *Chem. Weekblad* 16, 3-20, 328-42, 435-49 (1919).—Continuing his discussion of the relations between various physical consts. of liquids (*C. A.* 12, 2470) v. L. deduces a number of equations and uses them to interpret the data for benzene and fluorobenzene. L. H. ADAMS

The significance of Langmuir's and Harkins' theory of the orientation of molecules in the surfaces of liquids. R. T. A. MEES. *Chem. Weekblad* 16, 823-32(1919).—A detailed review of the investigations and conclusions of Langmuir and of Harkins on the nature of surface films. L. H. ADAMS

Thermodynamics of normal elements. VII. The temperature formula of the Weston normal element and the solubility curve of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$. ERNST COHEN AND J. J. WOLTERS. Utrecht. *Z. physik. Chem.* 96, 253-8(1920); cf. *C. A.* 13, 1038, 3059.—The soly. of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ has been measured and the following values (in g. CdSO_4 per 100 g. satd. soln.) have been obtained: 43.047 at -3.00° , 43.020 at -6.00° , 43.008 at -9.00° and 43.029 at -12.00° . The passage of the soly. through a minimum at about -9.00° is in agreement with Jaeger and Wachsmuth's temp. formula for the international Weston element: $E_t = E_{20} - 0.000038(t - 20) - 0.00000065(t - 20)^2$, since this formula gives for the soly. minimum a temp. of -9° . On the other hand, this temp. for minimum soly. deviates considerably from that derived from Wolff's temp. formula (cf. *C. A.* 2, 2505), $E_t = E_{20} - 0.0000406(t - 20) - 0.00000095(t - 20)^2 + 0.00000001(t - 20)^3$, which was adopted by the International Conference of Elec. Units and Standards (London, 1908). VIII. ERNST COHEN, W. D. HELDERMAN AND A. L. TH. MOESVELD. Utrecht. *Ibid* 259-74.—The chem. energy (E_c) of the Weston element with the solid phase $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ has been calcd. from thermochem. data. The quantity E_c is equal to the sum of the heats of reaction accompanying (1) the withdrawal of 1 g.-at. of Cd from the amalgam (W_1); (2) the union of this g.-at. of Cd with SO_4 to form CdSO_4 -anhydride (W_2); (3) the decompn. of 1 mol. Hg_2SO_4 (W_3); and (4) the conversion of the CdSO_4 -anhydride to solid $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ (W_4). The quantities $W_2 + W_3$, equal to the difference between the heats of formation of CdSO_4 and Hg_2SO_4 , and W_4 have been measured, while W_1 has been calcd. from Hulett's measurements (cf. *C. A.* 4, 857). It has been found that $E_c = W_1 + W_2 + W_3 + W_4 = -5675 + 45346 + 7890 = 47561$ g.-cal. This value agrees with those calcd. from the temp. formula of the Weston element; the Jaeger and Wachsmuth formula gives $E_c = 47427$ g.-cal., while the Wolff formula gives $E_c = 47447$ g.-cal. H. JERMAIN CREIGHTON

The Hall effect and the Nernst effect in magnetic alloys. ALPHRUS W. SMITH. Ohio State Univ. *Phys. Rev.* 17, 23-38(1921).—In the Fe-Cu series a max. Hall effect was obtained with 1.5% Cu. The variation with compn. is very similar to the variation of elec. resistance. In the Ni-Cu series the effect reaches a max. with about 26% Cu when the compn. corresponds to the formula CuNi_3 and then drops suddenly to a small fraction of its max. value. In the Fe-Ni series, although the effect is positive for Fe and negative for Ni, the effect increases linearly with the proportion of Ni added to Fe until for 13% Ni it is six times as great as for pure Fe. In certain alloys the variation of the effect with the field strength is anomalous, the effect being negative for weak fields and positive for strong ones. An explanation based on the theory of Borelius (*C. A.* 14, 2294) is suggested which assumes that in addition to the positive part of the effect which is proportional to the fields strength there is a negative part which reaches a limiting value for strong fields. The Nernst effect in the Ni-Cu series varies with compn. in nearly the same way as the Hall effect, reaching a max. for the compn. CuNi_3 . In the Fe-Ni series, the effect decreases with the addition of Ni, becoming 0 for about 2.2% Ni and positive for higher concns. With 13% Ni the effect is about five times as great as in pure Fe. It is suggested that the amt. and direction of the Hall and Nernst effects are detd. by the crystal lattices and the fields of force in the intramol. spaces. D. MACRAN

The thermal variation of the coefficient of magnetization of some anhydrous sulfates, and the theory of the magneton. PH. THÉODORIDIS. *Compt. rend.* 171, 715-7(1920).—Measurements were made of the sp. magnetization of the 3 anhydrous

sulfates: manganous, cobaltous, and ferric, in the form of powder sealed in glass or fused silica tubes, and at various temps. up to 575°. The data are based upon a sp. magnetization for water of -0.720×10^{-6} . The relation between the reciprocal of magnetization and temp. could be represented for each salt by two straight lines of nearly equal slope, joined by a curve. The middle of the "discontinuity" was at 275° for MnSO_4 and CoSO_4 , and 260° for $\text{Fe}_2(\text{SO}_4)_3$. The calcd. const. of the mol. field proved to be negative, although in the chlorides it is positive. The Curie point (imaginary) would come below zero abs. The calcd. number of magnetons is 29 for MnSO_4 , 25 for CoSO_4 , and 29 for $\text{Fe}_2(\text{SO}_4)_3$.

R. B. SOSMAN

Ozone, forest air and weather. HANNS FISCHER. *Naturw. Umschau Chem.-Ztg.* 9, 145-7 (1920).—The popular notions and chem. theories about ozone are reviewed. Observations during a period from July 17 to Sept. 21, in a forest locality but adjacent to moor lands, indicated that a strong odor of ozone in the atm. was followed by rain the next day.

L. W. RIGGS

The international classification of bibliography. J. H. FRYDLINDER. *Rev. prod. chim.* 23, 687-96 (1920).—A detailed discussion of international classification of bibliography by means of the decimal indexing system, which is universal and international and can be expanded indefinitely to meet all requirements. For libraries, etc., having other indexing systems, it may be used for indexing purposes, thus complementing without disturbing the other systems. The advisability of revising the inorg. chem. nomenclature in French and other Latin, and Slav languages is discussed, and also the general method of indexing in periodicals and for official patent literature.

A. P.-C.

Classification of data. The decimal system. D. H. WESTER. *The Hague. Pharm. Weekblad* 58, 27-34 (1921).—The Brussels modification of the Dewey decimal classification is explained and advocated. Abstract journals in particular should give each abstract a Brussels number. Several European periodicals (*Rec. trav. chim., Chem. Weekblad* and others) have adopted this practice for their leading articles.

JULIAN F. SMITH

A chart for the reduction of gas volumes. HANS G. SCHWERDT AND W. W. LOEBE. *Chem.-Ztg.* 44, 818-9 (1920).—An elaboration of Walther Ostwald's table for reducing gas volumes, largely mathematical. The chart will soon be placed upon the market by Stuga of Berlin.

J. T. R. ANDREWS

The production of artificial diamonds. FRANZ FISCHER. *Mülheim. Brennstoff Chemie* 2, 9 (1921).—Since electrically conducting carbon is formed only at temps. above 700°, and diamond is a nonconductor, F. concludes that Moissan's diamonds formed in the solid iron below 700°. He suggests that if an equally good solvent (as Fe) for C could be found, solidifying below 700°, conditions would be much more favorable for the formation of large crystals.

W. B. V.

Radiation as a factor in chemical action (LANGMUIR) 3. Acidity of Japanese acid clay (KOBAYASHI) 15. Molecular coefficient of refraction (EISENLOHR, WÖHLISCH) 10. The principle of the constant sum of energies of formation and their distribution on the unions in aromatic substances (STREIGER) 10. The leucoscope and its application to pyrometry (PRIEST) 1.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

GERALD L. WENDT

Twentieth century physics. R. A. MILLIKAN. *Smithsonian Report for 1918*, 169-84 (1920).—A popular lecture. The spirit of modern scientific inquiry is based

on 3 elements, a *philosophy*, a *method*, and a *faith*. M. outlines the ten most important advances in physics during the last 20 years as follows: The proof of the existence of the atom through Brownian movements; the proof of the divisibility of the atom; radioactivity; the atomicity of electricity; the elec. origin of mass; the discovery of the nucleus of the atom; of the nature of X-rays; examn. of crystal structure by X-rays; the discovery by Moseley that the sq. roots of the frequencies of the characteristic X-rays of the elements varied by steps changing by unity from one element to the next in the periodic table, and the discovery of quantum relationships in X-rays, photo-electricity, and optical spectra.

L. B. LOEB

The structure of atoms and molecules. Older and newer theories. I. TRAUBE. *Physik. Z.* 21, 592-7(1920).—T. attempts to show by means of data from some of his earlier papers that the van der Waal's equation of state, in spite of its inadequacies, is of considerable significance in the light of the newer at. and mol. theories of Bohr, etc. He shows that there is a const. relation between the mol. refraction of a large number of org. compds. and the sum of the "valencies" of the elements entering into these compds. A similar relationship is indicated between the mol. vol., or the const. "b" of van der Waal's equation and this sum of the so-called valencies. This holds very well for the elements of lower at. wt. But when elements such as I or Br are considered the values of the valencies that must be assigned to these are very high, 10 for Br and 17 for I in the first case. On the basis of this T. virtually introduces a new conception of valency, and therefore takes issue with the views of Kossel on the valency of atoms in compds. In analogy with the Bragg law for the absorption of α -particles by matter, he shows that the sum of the square roots of the at. wts. of the atoms in a mol. are proportional to the sum of the valencies in the mol. This leads him to conclude that while the total number of electrons in the mol. is roughly one-half the at. wt. the number of "valency" electrons in the atom is proportional to the square roots of the at. wt. He also discusses the question of the vol. of the H-ion in soln. and attempts to show that the size of the H-ion is of the same order of magnitude as those of Na and Li-ions in contradiction to the views of Kossel.

L. B. LOEB

Unanswered questions in atomic structure. A. SOMMERFELD. *Physik. Z.* 21, 619-21 (1920).—After briefly discussing the analogies between the different types of spectra possible for the H atom and for the alkali metals, S. shows that the spectra of the latter are much more complicated. The satisfactory interpretation of these complications in terms of an atom model has not been accomplished. He then discusses the possibility of an interpretation of these spectra in terms of the cubical atom. Introducing the equation for the potential energy of an atom having plane ring symmetry he indicates how this is changed in the case of an atom whose inner electrons have cubical symmetry. This condition demands that the first dimensionless constant term in the equation for plane symmetry become equal to 0. Now it is possible to evaluate the constant terms in the energy equation for the spectra of atoms where cubical symmetry should exist. This constant term is shown through the applications of the results of computations to a simple line of reasoning NOT to be equal to 0. This does not lead to the conclusion that the cubical arrangement is incorrect, but it only means that the cubes cannot remain symmetrical in the fields to which they are subjected. The cubes are distorted by the outer electron and thus make an electrical dipole or quadrupole with the nucleus, whose moment depends on the distance of the outer electron. This will bring other factors than the cubical terms into prominence in the expression for the potential, so that the result obtained above is not surprising. S. hopes with these concepts, and with an analysis of the arc and spark spectra that a clearer insight will be gained into the eccentricities and distortions of the cubes.

L. B. LOEB

The discovery of helium and what came of it. C. G. ABBOTT. *Smithsonian Report* for 1918, 121–6, Publ. 2550(1920).—A short historical account. N. F. H.

The constitution and structure of the chemical elements. HAWKSWORTH COLLINS. *Chem. News* 121, 219–22(1920); cf. *C. A.* 14, 1255, 2123, 2748; 15, 11.—The method described in *C. A.* 15, 11 is applied to most of the remaining heavy elements. A heavy element is believed to occur associated with its "constituent" lighter elements (e. g., Bi (209) = CoAs₈, AuC, ZnSb; Bi (207) = HPb, OsO, NaW, etc.). "Mineralogical facts" support the first assumption, not the second; therefore 209 is nearer the "true at. wt." of Bi than 207. Some difficulty is encountered with Zn (65) = KCN, but "Zn and KCN are both employed for dissolving silver and . . . are similar in several other ways." Some sp. grs. of Na and K compds. are calcd. from the sp. gr. of Na and K by a similar method. NORRIS F. HALL

The constitution and structure of the radioactive elements. HAWKSWORTH COLLINS. *Chem. News* 121, 243–4(1920); cf. *C. A.* 15, 11; and preceding abstract.—Guesses, in the vein of the preceding abstract (Ra = ZrBa = Ba—Ca—Na—Na—H—H₂, etc. Ti is the main ultimate constituent of U, Th, Io and Ra). N. F. H.

The charge on the atomic nucleus and the law of force. J. CHADWICK. Oxford. *Phil. Mag.* 40, 734–46(1920).—Hitherto the assumption that the nuclear charge of atoms is identical with the at. number has been without direct exptl. proof. The only means of studying the nuclear charge is through the scattering of α -particles. Rutherford has shown that if a pencil of α -particles falls on a thin sheet of matter, the number scattered which fall per sec. on unit area of a screen distant r cm. from the point of incidence of the pencil in a direction making an angle θ with it is given by $Qnb^2 \cos^4(\theta/2)/16\pi^2$, where Q is the number of particles per sec. in the original pencil, n is the number of atoms per unit vol. of the foil, t the thickness of the foil, $b = (2E/me^2)Ne$, where Ne is the nuclear charge of the scattering atom and m , e and v are the mass, charge and velocity of the α -particle. The detn. of N consists in counting the number of α -particles in the original and in the scattered pencil. Owing to the much greater number of the former, the exptl. enumeration by the same method in the two cases has not been practicable. A new device has been suggested by Rutherford to reduce the fraction of direct particles to the same order as that of the scattered ones, so that both can be counted through alternate intervals on the same screen. The device consists in cutting down the number of particles from the direct beam in a known ratio, by revolving a wheel with a slot opening which subtends a known portion of the total arc. The fraction is independent of the rate of revolution, but the time distribution can be conveniently regulated for counting by varying the speed. The results for Pt, Ag, and Cu were detd. as 77.4, 46.3 and 29.3, resp., where N is 78, 46 and 29, resp. Since the scattering was calcd. on the basis of the inverse square law of repulsion, the results prove its applicability in the region 10^{-11} cm. from the nucleus. The agreement between exptl. measurements of the K-series spectra and the theoretical values of Debye and Kroo shows that the inverse square law also holds at the K ring, which in Pt is about 10^{-10} cm. from the nucleus. Therefore measured at any point between 3×10^{-12} and 10^{-10} cm. from the nucleus the charge is equal to the at. number and the law of force is that of the inverse square, from which the conclusion is drawn that no electrons are present in the region between the nucleus and the K ring. S. C. LUND

The problem of radioactive lead. THEODORE W. RICHARDS. *Smithsonian Report* for 1918, 205–19, Publ. 2557(1920).—A reprint. See *C. A.* 13, 683, 1560. For subject matter, cf. *C. A.* 8, 3752; 10, 721, 2553; 11, 2, 1361; 12, 2063; 14, 1779, 3016.

NORRIS F. HALL

Protoactinium, its life-period and abundance in uranium minerals. O. HAHN. *Physik. Z.* 21, 591–2(1920).—The half-life period of Proto-Act may be estd. either by measuring the range of the α -particles, or by detg. the relationship to the calcd. equil.

activity of the total Proto-Act activity which arises in a known time in an initially Proto-Act-free U-prepn. The second method was here used. After blank tests had shown the possibility of sepg. added known quantities of Proto-Act completely from initially Proto-Act-free U salts with which they had been mixed, and also that the usual method of prepg. pure U salts completely frees them from Proto-Act, the Proto-Act content of 3 U preps., 20, 52 and 60 years old, resp., was detd. The half-life periods so calcd. were 12800, 11800, 12300 years. These agree within the exptl. error of 20%. Taking 12000 years as the best value, it is calcd. that the equil. ratio Proto-Act/U is 7.2×10^{-8} , or one ton of U in a mineral has associated with it 72 mg. of Proto-Act. Large scale extraction is under way, and it is hoped soon to obtain Proto-Act in "chemical" quantities for study.

NORRIS F. HALL

An electrical method for the measurement of recoil radiations. A. L. McAULAY. *Phil. Mag.* 40, 763-70(1920).—The recoil radiation produced by bombarding H gas with α -particles has been studied by Rutherford (*C.A.*, 13, 2480), the scintillation method having been employed. For certain reasons an elec. method would be more convenient. The attendant difficulties are due to the small number of swift particles to be counted and the interference of the high γ -radiation from the source of radiation. Ra C is employed as the source. The β -radiation is prevented from entering the ionization chamber by a strong electromagnet. The ionization due to the γ -radiation is compensated by a chamber of variable capacity in series with the leaf and so regulated as to oppose the charge from the direct γ -radiation, thus holding the leaf practically stationary. The α -ray source is so arranged that it can be exposed or turned off without affecting other conditions. The α -rays traverse a layer of H gas and are stopped by an Al screen which allows the recoil H radiation to pass into the ionization chamber. Except for a slight difference in range the ionization curve obtained is identical with that of the scintillation method, confirming the fact that in the repulsion which sets the swift H atoms in motion the nuclei do no act as point charges and that most of the H atoms are thrown straight forward.

S. C. LIND

The collection of radium emanation for therapeutic use. S. C. LIND. U. S. Bureau of Mines. *Science* 52, 640-1(1920).—It is proposed to simplify the app. and method employed in the collection of radium emanation, by abandoning the use of solns. and substituting a practice consisting in raising the dry salt *in vacuo* to the high temp. necessary to liberate the emanation in a state sufficiently pure to require no further treatment. The temp. for different salts of radium may lie above or below the fusion point of the salt. The use of a flux may be desirable in some cases. Elec. heating is suggested, which may be either internal or external.

S. C. LIND

Radioactive analysis of the thermal springs of Bagnères-de-Luchon, springs very rich in radium emanation. ADOLPHE LEPAPE. *Compt. rend.* 171, 731-3(1920).—The radioactivity expressed in millimicrocuries of emanation per l. of water, varied from 0.4 and similar low values for the potable springs to the very high values of 31.6 and 41.5 for two warm iron waters. There are fewer than ten places in the world with more active springs than these.

NORRIS F. HALL

The variations of the radioactivity of the springs of Bagnoles-de-l'Orne and their relations to rainfall. P. LOISEL. *Compt. rend.* 171, 858-60(1920); cf. *C. A.* 14, 1257. —The irregular variations previously found in the Nt content of these springs are shown by further study to follow the variations in rainfall for the most part. Certain irregularities, and the variations in the Ra salt content of the water, remain unexplained.

NORRIS F. HALL

The electron theory of the metallic state. G. BORHLIUS. Univ. Lund. *Phil. Mag.* 40, 746-63(1920).—An electron theory of the metallic state is developed, the assumption being made that the number of atoms is equal to the number of free electrons and that their special arrangement is the same as that of the Na and Cl atoms in the

face-centered cubical lattice, the electrons taking the place of the Cl atoms. On the basis of this theory B. discusses the potential energy of the metallic space lattice, the compressibility, the motion and kinetic energy of the electron at high temp., elec. cond. at high temp., thermal cond., ratio of conds., thermo-elec. phenomena, emission of electrons from hot metals, and magnetic and galvano-magnetic phenomena. The phenomena of elec. and thermal cond. at low and very low temps. are temporarily considered only in a qual. manner. S. C. LIND

Experiments on the nature of discharge of electricity through rarefied gases. S. RATNER. Univ. Manchester. *Phil. Mag.* 40, 785-93(1920).—The theory of the discharge of electricity through gases is still unsatisfactory with reference to the mode of initiation of the current. The object of the present paper is to investigate the validity of the idea that it is the stray positive ions which are drawn to the cathode with sufficient velocity to liberate electrons which then promote conduction through ionization by collision. A thin strip of Pt covered with Al phosphate was introduced into a vacuum tube provided with two other electrodes. By heating the Pt strip electrically it is made a rich source of ions, either positive or negative, according to whether it is made anode or cathode. It was found that positive ions impinging on the cathode under a fall of 2000 v. cannot liberate electrons from the surface of the cathode, nor did their presence materially alter the character of the discharge. The initial discharge is therefore not caused by the impact of positive ions. A method is described by means of which the stream of ions or electrons emitted from a hot wire in a vacuum tube may be isolated from the ions produced by collision within the tube. S. C. LIND

The pressure on the poles of an electric arc. A. M. TYNDALL. Univ. Bristol *Phil. Mag.* 40, 780-1(1920).—A note taking exception to some statements of Ratner (*C. A.* 15, 466) in regard to the effect of the elec. wind in producing pressure in elec. discharge through gases. S. C. LIND

Note on Einstein's law of additive velocities. W. R. MORTON. *Phil. Mag.* 40, 771-5(1920).—A graphical treatment of the application of the relativity theory to the law of the combination of velocities. Certain anomalies are pointed out and discussed which would arise were it possible to impart to matter velocity equal to that of light. S. C. LIND

Some optical effects including refraction and rotation of the plane of polarization due to the scattering of light by electrons. J. J. THOMSON. Cambridge. *Phil. Mag.* 40, 713-34(1920); cf. *C. A.* 15, 468.—T. continues his consideration of the scattering of light by electrons. With reference to refraction the usual equation of Drude is developed in a different way, but in addition T. shows that it holds only in case the electronic displacement is always in the direction of the resultant forces; when this is not so, it is possible for the electronic d. calcd. by this means to be 3 times that calcd. by the old formula. Equations relating the asymmetric structure of mols. with the magnetic rotation of the plane of polarization are developed. The mol. must be very unsymmetrical for the rotation to have a finite value. The rotation vanishes if the mol. has dynamical symmetry, or if the center of the elec. charges coincides with the center of mass, or if the principle axis of inertia coincides with axes of symmetry of the elec. charges, or if the elec. charges form a geometrically symmetrical system even though the masses might not be symmetrical, or if there is a plane of symmetry in the mol. The general conclusion is reached that optical rotation is produced by the electrons that couple the atoms to the central C atom. More complete knowledge of the absorption bands of org. compds. in the Schumann region is desired in order to ascertain the position of the various bonds from which rotation could be calcd. It is certain that the electrons cannot be at the corners of a regular tetrahedron, the arrangement usually assumed, which is not compatible with the theory of optical rotation. S. C. L.

Radiation pressure on electrons and atoms. LEIGH PAGE. *Astrophys. J.* **52**, 65-72 (1920).—Calcs. based on the classical electrodynamic equations show that the mean radiation pressure on a large number of at. oscillators is chiefly a resonance pressure. It is a function of the natural frequencies of the oscillators and of the ratio of wave length to at. diam. This resonance pressure has been neglected by several authors. The radiation pressure at the sun's surface is greater than the gravitational force, in the case of certain atoms of low at. wt. FARRINGTON DANIELS

Radiation as a factor in chemical action. IRVING LANGMUIR. *J. Am. Chem. Soc.* **42**, 2190-2205 (1920).—L. argues that the radiation hypothesis of chem. action (*C. A.*, **11**, 112; **12**, 2477; **13**, 3067) is invalid because (1) there are no absorption bands in H_2 and certain colorless gases at the frequencies predicted by the Trautz-Lewis-Perrin hypothesis. (2) The energy required for the monomol. decompn. of PH_3 (*C. A.* **13**, 2826) is shown to be much greater than the energy, as calcd. by the radiation laws, which can be supplied by the vessel walls at the calcd. frequency. (3) The heat cond. of H_2 , I_2 and N_2O_4 is shown to be much greater than for gases which do not dissociate. The laws which govern the temp. coeff. of a chem. reaction and the emission of monochromatic radiant energy are similar because they are both expressions of probability phenomena. A monomol. reaction is independent of mol. collision because the time between collisions is very great compared with the time of activity. Since the energy of activation cannot come from mol. collision nor from radiant energy emitted by the walls it must come from latent internal energy of the mol. L. assumes the trigger action by which energy of low intensity releases energy of high intensity. The photoelec. effect and other quantum phenomena are problems of a similar nature. FARRINGTON DANIELS

The X-ray spectra of tungsten. WM. DUANE AND R. A. PATTERSON. Harvard Univ. *Phys. Rev.* **16**, 526-39 (1920).—Measurements are tabulated for the critical absorption wave lengths of the K and L series and the emission wave lengths of the L series. A spectrometer similar to that previously described (*C. A.* **12**, 697) was used. With two slits to define the width of the beam of X-rays incident on the crystal and with the slit in front of the ionization chamber wide enough to admit the entire reflected beam, the wave lengths were calcd. from the angle through which the crystal turned. Spectra in the 1st, 2nd and 3rd orders were used and the method allows of a good estimation of the relative intensity, breadth, etc., of the various lines. The assumption of Sommerfeld based on the Bohr atom that if some of the orbits are elliptic in certain atoms and circular in others the K critical absorption frequency should be complex is not confirmed by these measurements which agree with those of Duane and Shimizu (*C. A.* **13**, 3073). Also if this assumption is true, the difference between the K absorption frequency and one of the L absorption frequencies should not be equal to a $K\alpha$ emission frequency, whereas these measurements show that this equality does exist within the very small expl. error. The effect of different kinds of atoms is too small to be detected for the heavier elements. By the use of one of the quantum equations Sommerfeld has calcd. for the Bohr atom the eccentricity of the elliptic orbit from which he gets an expression for the frequency of the L series doublet. This expression contains an undetd. const. to which S. has assigned a value 3.63 calcd. from the published values for L series of different elements. This expression fits the data described in this paper within 1%. F. O. A.

Absorption lines in X-ray spectra. G. HERTZ. *Physik. Z.* **21**, 630-2 (1920).—H., in agreement with Kossel's prediction (*C. A.* **15**, 629), has already found (*C. A.* **15**, 206), indications of a fine structure for the critical absorption frequencies of the L series, $N = 55$ to 60. The work is now repeated, using a slit only 0.002 Å. wide. With such a thin layer of absorbing substance that the continuous absorption above the critical absorption frequency can scarcely be detected, a sharp absorption line appears just

above the emission frequencies. It has the same width, approx., as the slit (equiv. to a few v.), and is to be interpreted as indicating an electron transition from the L ring to the first ring outside the valency ring, thus corresponding to the first resonance potential of ordinary spectra. The complete X-ray absorption spectra will probably appear only in the case of monatomic gases.

R. T. BIRGE

Negative molions and the spectra of helium. FRANZ SKAUPY. Berlin. *Z. Physik.* 3, 175-7(1920).—There are some advantages in assuming the existence in the inert gases of negatively charged groups of atoms, called *molions*. In the case of He it might account for the similarity of its line spectra with that of the alkali metals, and the large moment of inertia might explain the absorption in the infra-red.

F. C. HOYT

A principle of selection and a theory of displacement in spectrum series. W. KOSSHEL AND A. SOMMERFELD. *Ber. physik. Ges.* 21, 240-59(1919).—The authors accept Bohr's assumption that spark spectra are emitted by ionized, arc and flame spectra by neutral atoms; they are led to the conclusion that the spark spectrum of an element corresponds to the arc spectrum of the preceding element in the periodic table. The spark spectrum will consist of doublets, triplets, or lines not apparently arranged in series, according as the arc spectrum of the preceding element is made up of doublets (as in alkalis), triplets (alkali earths) or lines having no apparent series arrangement (rare gases). This is worked out in detail for the above groups and the relations of the spectra are clearly shown. A principle of selection is given from which may be deduced the combinations of terms which can occur under ordinary conditions and those which can be forced only by powerful fields. The s-term is held to belong to the azimuth quanta-number $n = 1$. The doublets of the alkaline earths are spark spectra; their character as a doublet system is explained by the doublet character of the arc spectra of the alkalis. Between the arc spectrum of an alkaline earth and an arc spectrum of the immediately preceding alkali, simple numerical relations exist. The spark spectra of the earths are triplet systems of the same character as the arc spectra of the alkaline earths. A definite relation exists between a triplet in the spectrum of an earth and the corresponding triplet of the preceding alk. earth.

C. S. BRAININ

The absorption of light by the Goldberg wedge. F. C. TOY AND J. C. GHOSH. Univ. Coll., Lond. *Phil. Mag.* 40, 775-80(1920).—The extinction of the Goldberg wedge (*C. A.* 5, 3543) which consists of an emulsion of lampblack in gelatin has usually been assumed to be const. for all wave lengths without any exptl. evidence. An investigation of the variation has been made between 660 and 290 μ . The results show that the particular type of wedge used has practically const. extinction throughout the visible spectrum, but that there is a very pronounced departure in the ultraviolet region normally used in photographic research. The departure is in the direction of increase of "photographic density" with decreasing wave length in an abnormally high ratio in the ultraviolet region.

S. C. LIND

Elements in the sun (paper B). MEGH NAD SABA. Univ. Coll. Sci., Calcutta. *Phil. Mag.* 40, 809-24(1920); cf. *C. A.* 15, 468.—The theory of temp. ionization of the elements developed in Paper A by S. is made the basis for explaining the presence or absence of many of the solar spectral lines. If the temp. and pressure at which ionization takes place are known and if the lines characteristic of the atom or of the ion are known, the interpretation of results is greatly aided. Of the alk. metals, K, Ca and Rb would be completely ionized in the sun; no lines have been observed in the solar spectrum though they are abundant in the arc spectrum. The case of Na is of especial interest. At a temp. of 7500° K. Na is 60% ionized under conditions corresponding to the photosphere, but completely so when the pressure falls to 10^{-7} atm. which agrees with the exptl. observation that the D₁ and D₂ lines reach only a certain level above which height only ionized Na is present, the chief emission of which lies in the extreme ultra-

violet and escapes detection. Applications of the theory are also made for the elements Mg, N, and He. The case of the unidentified Fraunhofer lines is also discussed.

S. C. LIND

Inorganic luminescence phenomena. I. Effect of crystalline form, flux and actual melting on phosphorescent zinc sulfide. ERICH TIEDE AND ARTHUR SCHLESSE. *Ber.* 53, 1721-5(1920).—The crystal form of ZnS had no effect on its phosphorescent properties. Neither sphalerite nor wurtzite prepared with great care from pure materials ($Cd < 10^{-4}$) was phosphorescent unless it was either (a) actually melted, or (b) heated for some time with at least a trace of a flux such as KCl. Both forms showed phosphorescence when treated in either of these ways. Pure fused alkaline earth sulfides were also phosphorescent. The favorable action of the flux, therefore, does not depend on its favoring the formation of a particular crystalline variety; it must actually intermolecularly raise the vapor pressure and lower the melting point of the sulfide.

NORRIS F. HALL

The phosphorescent oxides of calcium, strontium, and barium. FERDINAND SCHMIDT. Heidelberg. *Ann. Physik* 63, 264-94(1920).—Ternary mixts. were prepd. by heating an alk. earth (CaO, SrO, BaO) with a small amt. of a fusible substance (NaCl, NaF, Na_2HPO_4 , CaF_2 , MgF_2 , Li_3PO_4 , KH_2PO_4 , $K_2B_4O_{10}$, etc.) and a trace of a nitrate (of Cu, Mn, Bi or Pb), in a gas oven to temps. varying from dull-red to yellow heat. The mixts. were illuminated with visible and ultraviolet light, and any phosphorescence was noted. The light-source was a condensed subaqueous Al spark which gave a continuous spectrum to a wave length of 220μ . Light from the spark passed through a quartz prism and fell upon the powdered specimen which lay on an electrically heated stand calibrated in terms of the wave length of the incident light. Three different types of secondary radiation (phosphorescence) were observed in many of the preps., differing in duration, but all of the same wave length for any particular mixt. The most persistent and interesting after-glow was usually excited by from 2 to 4 distinct bands of incident light, having their intensity-maxima, in a typical case, at $\gamma = 215, 271, 336$, and 400μ . The secondary radiation was in all cases a single band (or by changing the method of preparing the mixt., could be sepd. into single bands) corresponding to a particular set of bands of exciting (primary) light. Cathode rays and ultraviolet light excited the same phosphorescence from any given mixt. The color (spectral frequency) of the phosphorescence band varied broadly with the compn. of the mixt., and within narrow limits for each particular mixt. with (a) the method of its prep., and (b) its temp. during emission. Most of the mixts. if illuminated at low temps. did not glow, but having been so treated, became brightly phosphorescent on heating to $300-400^\circ$, whether the incident light was cut off or not. Even keeping a previously illuminated salt for days at low temp. did not prevent its glowing brightly when subsequently heated. The phosphorescence always had a longer wave length than the incident light. Ca, Sr and Ba in their oxide compds. mixed with the same activating metal oxide show phosphorescence of increasing γ (e. g., $CaOCu$ blue, $SrOCu$ green, $BaOCu$ yellow). The oxide, sulfide and selenide of a particular metal show progressive increase in the γ , both of the phosphorescence and of the effective exciting light. They also show a progressive decrease in the minimum temp. at which they glow brightly. It is believed that these results indicate a smaller dielec. const. in the oxides. Some work by other investigators has been included in this summary.

NORRIS F. HALL

The phosphorescent sulfides and their applications. A. A. GUNTZ. *Chimie & industrie* 4, 597-611(1920).—A general review of the history of the phosphorescent sulfides, the theories advanced to explain their action, their principal properties, and the various industrial applications to which they have been put, including those de-

pending on the action of ultraviolet light, X-rays, Ra and other radioactive substances, and light.

A. P.-C.

Experiments on the possible influence of potential difference on the radiation of the resistance furnace. ARTHUR S. KING. *Astrophys. J.* 52, 187-97 (1920).—This investigation was undertaken to det. whether or not the currents through the ionized vapor, produced by a potential gradient of 1 or 2 v. per cm. along the heating tube, were responsible for the emission of some of the furnace lines, a view held by Hemsalech. Four different methods were used to eliminate these currents, or to discount their effects. A protected tube was installed and heated by d. c., thus giving the same temp. with a smaller potential gradient than that required when the unprotected tube and a. c. are used. The spectra were identical at the same temp. An inner tube was insulated from the heating tube by means of cooled quartz, so that there could have been no current through the luminous gas. In this case also the spectrum was the same at the same temp. The spectra were also photographed by exposing, after the current had been shut off, and the sensitive lines were found to be of the same relative intensity as if the current had been on. Finally, the tube was heated by an external arc and this arrangement gave the same spectrum as that of the tube operated by a. c. at considerable voltage. It is concluded from these expts. that the lines are due to the temp. and that no low voltage arc through the gas is necessary. Each temp. gives a definite spectrum. The "red fringe" observed by Hemsalech is probably a chem. phenomenon, similar to a flame. It may be obtained when no p. d. is acting on the vapor. K. BURNS

Blue sky and the optical properties of air. LORD RAYLEIGH. *Proc. Roy. Inst. Gl. Britain*, Preprint May 7, 1920.—This address gives a review of the work of the speaker and his father on atm. scattering of light and the absorption of O_3 . It will be of particular interest to those who may wish to show these phenomena to a class. A soln. of $Na_2S_2O_8$ was decompd. by an acid and the light scattered by the resulting particles was shown to be richer in blue than the incident light. By polarizing the incident light the scattered light was shown to be polarized. The dust was filtered from a tube of air and the ordinary luminosity of a beam of light was shown to disappear. But by taking pains to screen extraneous illumination it has been possible to see the light scattered by the mols. and to show its polarization. The polarization of the sky was discussed and it was shown that the polarization of the night sky can be found by photography, making use of a Savart polariscope. The night sky is not so strongly polarized as the day sky; still the effect is certainly measurable. The weakness of the polarization shows that the light in the night sky is not due to sunlight scattered by a high atm. It was shown that the blue color of the sky could not be due to absorption of O_3 . But the limiting of the ultraviolet end of the solar spectrum was shown to be due to O_3 . The effect of this absorption was demonstrated by means of a beam of light projected upon a screen of barium cyanoplatinate by a quartz spectroscope. By passing a part of the ray through a tube containing O_3 the extreme ultraviolet was cut off. Many years ago a group of bands was found at the limit of the stellar spectra. The speaker and his associates succeeded in observing these bands in the solar spectrum, and proved in the lab. that they were due to O_3 . By photographing the spectrum of a Hg lamp at a distance of 4 miles it was shown that O_3 is not a constituent of the air near the surface of the earth, but is confined to the upper air. K. BURNS

Protection of medicines against the action of light (CORBERGH) 17. Relationships between radium and life (KOBLSCH) 11A. Radium from a pharmaceutical point of view (RENNEBOOG) 17. Table of rays of great sensitiveness of the elements for use in analytical research (GRAMONT) 7. Deduction of the dissociation-equilibrium from the theory of quanta and a calculation of the chemical constant based on this (ZEHNFEST, TREAL) 2. The fundamental constants of nature (COLLINS) 2.

Radium luminous coatings. E. O'HARA. U. S. 1,364,950, Jan. 11. Watch or clock dials or similar articles are enameled, luminous markings are applied over the enamel and the markings are covered with a protective coating free from Pb and vitrified on the luminous surface. U. S. 1,364,951 relates to a similar method of prepping luminous dials in which the luminous material, *e. g.*, Zn sulfide and RaBr_2 , is mixed with a reflux or glaze which is fired or vitrified on the surface after application as a coating or marking. The glaze may be a potash lime glass.

4—ELECTROCHEMISTRY

COLIN G. FINK

Arthur Edwin Kennelly. ANON. *Elec. World* 77, 356(1921); 1 illus.—Brief biographical sketch. C. G. F.

Electric furnace has proved value. CARL H. BOOTH. *Foundry* 48, 994-7, 1004 (1920); illus; cf. C. A. 14, 495.—Description and operating records of a rotating elec. brass-melting furnace. See C. A. 15, 23, 470.

LOUIS JORDAN

Three-phase electric brass furnace of novel design. ANON. *Can. Chem. J.* 4, 315(1920).—The Volta Mfg. Co., Ltd., of Welland, Ont., has developed and put on the market a 3-phase elec. brass furnace in 500-, 1000-, and 2000-lb. sizes with power ratings of 125, 175 and 300 kw., resp. The furnace shell is an upright cylinder mounted on a cast-Fe base provided with a motor-driven set of gears and rollers which give a gyratory movement to the furnace. One of the features of this furnace is that it is a 3-phase unit, which means a balanced load on the power company lines and consequently a better power rate to the operator. Three graphite electrodes, provided with water-cooled collars, enter the surface through the sides of the shell at points 120° apart. Provision is made for changing the position of the electrodes relative to each other as well as for raising and lowering them in respect to the metal bath. The charging door is below the level of the electrodes and it is not necessary to withdraw the electrodes from the furnace during either charging or pouring. The nature of the arcs and the motion of the furnace prevent overheating of the bath and reduce volatilization losses. Power consumption on yellow brass has been as low as 225 kw. hrs. per ton of metal produced; for Al-bronze the av. was 300 kw. hrs. per ton. These figures were not for continuous operation.

LOUIS JORDAN

Performance of electric furnaces. ANON. *Engineering* 110, 742(1920).—An account of costs for the first 50 heats from a 6-ton Greaves-Etchells elec. steel furnace installed at the Mare Island Navy Yard. The conditions for these heats were not favorable in that the plant was new and only one heat per day was run. The av. time per heat was about 5 hrs. The ladle loss of metal was 3.18% of the material charged to the furnace. The electrode consumption (omitting the first 10 charges) was 19 lbs. per ton of material charged. Itemized operation and maintenance costs are given. The totals are \$36.58 for operation and \$4.04 for maintenance per ton of material charged. This does not include cost of supervision nor allowance for depreciation. These items would probably bring the cost per ton under continuous operating conditions to something less than \$58.

LOUIS JORDAN

Swedish electric pig iron furnace. JONAS HERLENIUS. *Chem. Met. Eng.* 24, 108-12(1921).—The first Swedish elec. pig-Fe furnace was installed at Domnarvret in 1909. On the basis of the results obtained with this furnace a special trial plant was built in 1910 at Trollhättan. Trials conducted at this plant for nearly 2 yrs. were very satisfactory. At the present time a total of 12 of these furnaces ranging in size from 2,200 to 8,000 kv. a. are in operation in plants in Sweden. Similar furnaces are in operation or contracted for in Norway, Italy, Japan and Brazil. The furnace consists

of a wide melting chamber or crucible above which is a shaft with a bell-charging apparatus at the top. The shaft is designed in accordance with the general practice for common blast furnaces except for a recent tendency to widen out the lower section, making the diameter of the shaft at its junction with the crucible even larger than at the bosh. The entire brickwork and shell-plate of the shaft are suspended independently of the crucible and make a flexible, water-cooled joint with the roof of the crucible. The shaft is lined with firebrick to a thickness of 18 in. for the upper and middle sections and about 14 in. for the lower. The crucible is cylindrical and is usually lined with firebrick, although rammed-in coke and waste electrodes have been used with success. The crucible roof is of firebrick of special shape. Through this roof the electrodes are inserted at an angle of 65° with the horizontal. A portion of the waste gas taken from openings in the throat is returned to the furnace and forced into the space between the charge and the roof through tuyères which point upward to blow the gas directly underneath the roof in order to cool it. The vol. of the circulating gas is const., so the gas formed during the process is available for auxiliary heating. This gas has a high B. t. u. value (258 B. t. u. per cu. ft. dry gas). The electrodes are of amorphous C, 4 to 8 in. no., round (24 in. in diameter), and jointed for continuous feed. Electrode consumption has varied from 11 to 19 lbs. per ton of pig produced. As the power input is regulated by changing the transformer voltage, there is no need for electrode adjustment, except as they are consumed. The electrode holders, elec. contact clamps, the flexible joint between shaft and crucible, the tap-hole, and the tuyères are all water-cooled. There is a water-spray device for the entire shell of the crucible and the crucible roof is cooled by an air blast. The necessary elec. equipment is described. The transformer secondary voltages required for operating are 55–110 v. for charcoal or 35–70 v. for coke furnaces. There are installations operating on 25- and 50-, as well as 60-cycle a. c. In starting the furnace it is pre-heated for 2 to 3 weeks with a wood or coke fire in the crucible. Then 2 to 3 tons of coke and about 20 charges of coke, ore, and lime are shoveled into the crucible through the electrode holes and the electrodes inserted. The shaft is filled with mixed ore, lime and coke, and finally with charcoal with slowly increasing ore content. The current is then switched on, but the gas circulation is not started until about 2 days later. The charges contain 50–60% of Fe. The consumption of charcoal amts. in general to only 35–40% of the requirement in a common blast furnace. During 1918 the av. consumption of charcoal in all Swedish blast furnaces was 55.6 hl. per ton of pig, whereas in the elec. pig-Fe furnaces it amounted only to 24.8 hl. per ton. Few data are available as to the operation of these furnaces on coke (Stig, *C. A.* 14, 2752) Elec. pig-Fe is more thoroughly deoxidized than pig from the common blast furnace and, therefore, requires less Si and Mn to be suitable for the open hearth. Fe and slag are tapped from the elec. furnace at a lower temp. than from the blast furnace, but with an ample power input the temp. can be increased. There is no trouble in producing a pig high in C and Si and with a gray fracture. Desulfurizing in usual practice is less than in the ordinary blast furnace, owing to the lower temp. This is overcome in recently installed high-power furnaces. About 2800 kw. hrs. are consumed per metric ton of pig-Fe produced. L. JORDAN

Heat modifies acid furnace reaction. J. W. GALVIN AND C. N. RING. *Foundry* 49, 72–4 (1921).—The acid elec. steel furnace in foundry practice is considered. The efficiency of the furnace depends largely on the method of building up the bottom and the shape of the bottom. It should be burned in layer by layer and should have steep sides (cup-shaped rather than saucer-shaped) in order that the charge, both before and after melting, may be more directly under the arcs and subjected in larger part to direct flow of the current and, therefore, heated by internal resistance of the metal rather than by radiation from the arc and conduction from the center of the bath alone. Time and current can also be saved by using scrap that forms a compact mass. When

such scrap is not available it is of advantage to leave some liquid metal in the furnace after each run and as quickly as possible throw in the new charge. The whole mass will then tend to weld into a solid body. After the charge is molten the slag should be kept thin by the addition of small amts. of Fe-ore from time to time. The control of the Si content of the product of the acid elec. furnace is most difficult. At the temp. of the open-hearth furnace SiO_2 is not reduced by C, but at the higher temp. of the elec. furnace this reaction does take place and the Si is absorbed by the metal bath. It is probable that Fe also has a reducing effect on SiO_2 under these conditions. This trouble is avoided and oxidation of the metal is kept down by holding the temp. of the metal to open-hearth temps. until the furnace reactions are as nearly complete as possible and then rapidly increasing the temp., and tapping at once before the high temp. reactions have time to go very far.

LOUIS JORDAN

Electric cast-iron pipe. ANON. *Iron Age* 106, 1542(1920).—The conviction has been established for some time that cast-Fe pipe should be light-weight. It is the light-weight cast-Fe pipe of early days that has given the best service records. Previous to the war the low cost of both pig-Fe and transportation led to putting more Fe in the walls of pipe to increase the factor of safety in founding. With advancing prices, the cost of pig-Fe became the big factor in the cost of cast-Fe pipe. A lighter product was made by using the elec. furnace for the treatment of cupola-melted Fe. A mixture sufficiently low in C and Si to result in a tenacious Fe can be raised in the elec. furnace to a sufficient temp. to make thin-section castings and at the same time clean the Fe of impurities. The product shows a tensile strength of 30,000–40,000 lbs. per sq. in., and a transverse strength (in the standard 2-in. by 1-in. bar) of 26,000–35,000 lbs., with a deflection of 0.38 to 0.50 in.

LOUIS JORDAN

Electrolytic zinc plant of Anaconda Copper Mining Co. at Great Falls, Mont. FREDERICK LAIST, F. F. FRICK, J. O. ELTON AND R. B. CAPLES. *Trans. Am. Inst. Mining Eng.* No. 1028, 55 pp.(1920).—A very comprehensive description is given of the methods developed for recovering Zn from concentrates high in Fe and Pb. The oxide roast in Wedge furnaces was adopted, and later the sulfate to make the plant self-supporting in acid. Provided temp. is kept low, about 82% of the total Zn in the calcine is easily rendered sol. in 2% H_2SO_4 . The leaching is done in Pachucas with cell acid; in the 1st stage $\frac{3}{4}$ of sol. Zn is extracted, and by subsequent treatment: (1) Fe is oxidized and pptd.; (2) gelatinous SiO_2 is coagulated and rendered granular; (3) As and Sb are completely pptd.; (4) 80% of the Cu is pptd. by excess base. When properly carried out each granular particle appears enclosed in freshly pptd. Fe, CaO or SiO_2 , and thus provides the wt. to carry down the flaky particles. The 2nd stage, where residues (50% solids) are treated with the rest of the cell acid and discharged at 0.5% acidity to settle, includes: (1) soln. of remaining sol. Zn and Cu; (2) final sepn. of solids from Zn-Cu soln.; (3) roughing out of Cu and Cl; (4) soln. of sufficient Fe to remove all As and Sb in neutral leach; (5) elimination of the As and Sb partly redissolved in dil. acid. Purification of the neutral soln. is effected by adding Zn dust in excess for pptn. of all Cu and Cd. Failure to realize harmful effects from mere traces of impurities prevented success of early expts. A rotary converter supplies current for electrolysis; 28 anodes of chem. Pb and 27 cathodes of sheet Al, $2 \times 3\frac{1}{2}$ ft. $\times \frac{3}{16}$ in., are used per tank with 2-in. spacing. After 2 days run Zn is stripped from each side of the cathode. At 30 amp. per sq. ft., the p. d. is 3.8 v. per cell and about 11 lb. of Zn is obtained per h. p. yr. At 2-hr. intervals glue is added to the bath (1 to $1\frac{1}{2}$ oz. per ton of metal), giving a dense deposit better suited for melting. No way has yet been devised to prevent slight corrosion of Al sheets above the soln. line. The Zn-casting plant contains 2 coal-fired reverberatories of 100–125 tons capacity each; a 200-ton elec. furnace was discontinued after 6 mo. trial. About 4–5% of cathodes forms in dross. About 8% goes to the atomizing plant to make the Zn dust required. Residues

are now treated to slag as much Zn as possible and give a rich leady mat. Illustrations are numerous and very well selected.

F. H. HOTCHKISS

A new high-capacity storage battery. C. W. HAZLETT. *Trans. Am. Electrochem. Soc.* 39, preprint (1921).—Storage battery capacity depends on little else but active surface, so that grid thickness ought to be reduced as nearly as possible to the depth of the active portion, *i. e.*, about $\frac{1}{32}$ in. This has been accomplished by punching grids out of extra thin sheet Pb-alloy $\frac{1}{32}$ in. thick instead of *casting* grids of a possible minimum thickness of $\frac{1}{8}$ in. Since the porous fiber separators have surfaces flush with the grids, erosion and the escape of active material from the plates are prevented. Since the current flow per unit area is less than in present standard plates due to increased area, the chemical and physical deterioration in service and in charging is greatly lessened. Grooves in the separators are not necessary for circulation of electrolyte; during charging the gas escapes readily and no channels are provided; good capacity is retained at high discharge rates; separators do not clog; separators hold enough electrolyte for complete discharge; plates are packed tight and cannot buckle. The performance of this new H. battery, on the unit wt. basis, is from 50 to 200% above that of standard types.

F. H. HOTCHKISS

Booster saves energy in charging storage batteries. L. R. WEST. *Elec. World* 77, 264 (1921).—The current from discharging batteries is used to charge other batteries. A booster allows the batteries to be discharged back into the line and reduces the size of the generator required for charging. An example is cited where a saving of 15% in kw. is obtained.

L. P. ÖHLIGER

Review of recent (German) patents on dry cells and batteries. HANS BOURQUIN. *Elektrochem. Z.* 27, 21-4 (1920).

C. G. F.

Discharge through an aluminium-cell lightning arrester. HIDETSUGU YOGI AND TAKASHI ONO. *Technology Reports Tohoku Imp. Univ.* 1, 161-76 (1920).—The Al-cell is believed to be most nearly ideal for protection of extra high-tension transmission systems, but very little is known of the conditions of breakdown or discharge. The electrode surface is covered with an O_2 gas film, partly converted into Al_2O_3 ; outside the gas layer there is a slimy film of $Al(OH)_3$. Thus a series of resistances and capacities is formed. Expts. were carried out to obtain the dynamic characteristic (curve of instantaneous voltage *vs.* amperage) of the discharge, especially at higher frequencies. The curve is nearly an ellipse at 250-1000 cycles per sec. Interpretation of the characteristics at these frequencies shows very desirable qualities for lightning arresters: (1) the condenser action of the film makes the charging current increase with frequency; (2) the discharge has less tendency to cause recurrent surges; (3) reforming the film takes an appreciable time so that the discharge current may continue without disruptively puncturing it.

F. H. HOTCHKISS

The optophone (selenium cell). FOURNIER D'ALBÉ. *Electrician* 86, 79-80 (1921).—As alternative of raised-type systems and also to enable reading of ordinary print by the blind, this device is put on the market. The page is fixed face-downward on a curved glass plate, under which oscillates an optical system on a rocker arm. The image of a small straight filament is focused in the plane of a perforated rotating disk radially across its circles of holes. The light falls on the printed matter as 5 bright spots or "scala," each pulsating according to the velocity and perforations of the disk. In series with a battery and telephone receiver is a Se cell or bridge which receives only light reflected from the page. Thus the intermittent illumination of the Se cell gives a note for each spot, and the sound is an indication of the particular letter. Black sounding, *i. e.*, white as silence, is obtained by using a second Se cell directly activated but connected to oppose the main cell. By adjusting the relative p. d. the telephone is silent when all "scala" are white and corresponding notes are sounded as they move over black letters.

F. H. HOTCHKISS

Some recent developments of high-current arcs. J. P. YORKE. *J. Inst. Elec. Eng.* 58, 651-60(1921).—A system is described for controlling the arc by acting upon it in all directions perpendicular to the axis of the carbons by a system of electromagnetic forces, which is adjustable in space. This is accomplished by an arrangement of 4 bare Cu conductors, one above, one below, and one on each side of the axis, all in series with each other and the arc. In this manner the arc stream is urged toward the center, and it has so been found possible to maintain a steady arc between carbons of smaller diam. than hitherto. The central core of the positive carbon can also be dispensed with. With a c. d. of 0.31 amp. per sq. mm. the crater diam. is nearly as great as that of the positive carbon. Methods for making tests of searchlight beams in the open at ranges of not less than 13,000 ft. are described. All impregnated carbons tested gave flames of greater luminosity than plain carbons, but they also produced a smaller flux of light in the beams, probably due to the absorptive effect of the fumes emitted by the former and to the reflective and absorptive properties of the flame itself.

W. E. RUDER

Simple board for testing small (electrochemical) equipment. A. H. PLATT. *Elec. World* 77, 380(1921).—Illustrated account of a small switch and testing board used for storage battery charging, testing ammeters, exptl. d. c. work, etc. The amperage range is 0.36 to 10.9; the resistance range 303 down to 10 ohms. Six lamps are used as resistance units.

C. G. F.

Electrical equipment and installation for laboratories. ANON. *Elektrochem. Z.* 27, 33-5(1920); 4 illus.

C. G. F.

Some electrical causes of dust explosions (PRICE) 24. Power from German peat (BARTEL) 21. The manufacture of tin-plate and the electrolytic detinning process (VIE) 9. Electrolytic iron (Vo) 9. Lighting in theory and practice (BUSH) 21.

Electric primary battery. F. R. PARKER. U. S. 1,366,095, Jan. 18. Structural features.

Storage battery. R. W. WALES. U. S. 1,366,223, Jan. 18. The separators of the battery are formed of cloth or paper impregnated with a synthetic gum to render them resistant to acid. The gum of U. S. pat 1,251,863 (C. A. 12, 780) may be used.

Storage battery. E. LAMAIRE. U. S. 1,366,010, Jan. 18. Structural features.

Storage battery. I. H. LEVIN. U. S. 1,366,090, Jan. 18. Structural features.

Storage battery. J. M. FRISS. U. S. 1,366,070, Jan. 18. Structural features.

Storage battery electrodes. J. M. ALLEN. U. S. 1,365,880, Jan. 18. Structural features.

Dry-cell electric battery. H. M. KORETZKY and B. H. TEITELBAUM. U. S. 1,366,191, Jan. 18. Structural features.

Dry-cell electric battery. G. FULLER, L. FULLER and G. J. A. FULLER. Brit. 152,818, Aug. 13, 1919. A dry cell contains a non-hygroscopic excitant such as NH_4Cl in a dry state mixed with a dry absorbent such as tragacanth or tapioca. When the cell is required for use, H_2O is added, causing the materials to gelatinize. A small quantity of ZnCl_2 may be added to the depolarizing material, the mixt. being dried before the cell is sealed. Cf. 102,294 (C. A. 11, 559).

Electrolyte for dry-cell electric batteries. B. H. TEITELBAUM. U. S. 1,366,298, Jan. 18. An electrolyte for dry batteries is prepd. by dissolving NH_4Cl 53.5 parts in 100 parts of a soln. containing 26.36% ZnCl_2 , filtering the soln. and adding flour and starch.

Depolarizer for galvanic cell. P. BURGER. Can. 208,081, Feb. 1, 1921. A depolarizer for galvanic cells comprises a mixt. of MnO_2 and finely divided chemically pure C in the form of soot.

Electrodes. HUGH B. CONOVER. Can. 208,903, Feb. 22, 1921. A tubular electrode for collecting fine dust from gases is combined with a discharge electrode in axial alignment therewith, which comprizes a metal rod with a plurality of metal disks fastened in spaced relation on the rod and the peripheral edges of the disks are rounded to increase the discharge surface of the edges.

Electrolytic process for cleaning electrodes. K. S. GUITERMAN. Can. 208,484, Feb. 15, 1921. Electrodes coated with deposits of metal such as Co are cleaned by utilizing the coated electrode as the anode of an electrolytic cell, containing an electrolyte sufficiently acid to prevent the deposition of the metals dissolved from the electrode and passing a current through the cell.

Negative plates for electric batteries. A. POUCHAIN. U. S. 1,364,953, Jan. 11. Negative battery plates are prepd. by placing an amalgamated Zn plate in an aq. bath slightly acidified with H_2SO_4 containing MgSO_4 and HgSO_4 , making the plate a cathode for some time in the bath, then drying it with gentle heating and wrapping it in an adhering sheet of paper. This treatment serves to obviate loss of Zn when the circuit is open and to give the plates good durability.

Electrolytic cell. M. A. ADAM, J. STEVENSON, J. FIELDHOUSE and A. T. MABBITT. U. S. 1,365,140, Jan. 11. The cell is adapted for deposition of metals in non-coherent form. It comprizes a rotatable cathode and a hollowed-out anode, in which the cathode may be rotated, and is provided with passages through the anode and casing for circulation of the electrolyte. The app. may be used for recovery of Sn from solns. containing Fe chloride also.

Electrolytic filter-press cell adapted for treating brine. L. E. WARD. U. S. 1,365,875, Jan. 18. Structural features.

Apparatus for purifying gases by electrical precipitation. G. A. KRAUSE. Can. 208,734, Feb. 22, 1921.

Apparatus for the electrical precipitation of suspended particles from gases. WALTER A. SCHMIDT. Can. 208,861, Feb. 22, 1921. The discharge electrodes of the pptg. app. consist of vertically extending rigid smooth bars or rods of metal.

Electrolytic apparatus adapted for recovering copper from ore-leaching solutions. W. E. GREENAWALT. U. S. 1,365,032, Jan. 11. The electrolyte flows through a sinuous path from the inlet to the outlet of the cell and at intervals in its path of flow it is sprayed into the layer of gas overlying the electrolyte in order to reduce $\text{Fe}_2(\text{SO}_4)_3$ in the electrolyte by the SO_2 in the upper portion of the app.

Electrolytic apparatus adapted for copper refining. W. E. GREENAWALT. U. S. 1,365,033, Jan. 11. Structural features.

Electrolytic apparatus adapted for copper refining. W. E. GREENAWALT. U. S. 1,365,034, Jan. 11. Structural features.

Electrolytic manufacture of metal capillary tubes. D. E. BATTY, S. WHYTE and ASSOCIATED EQUIPMENT CO. Brit. 153,231, Apr. 28, 1919. Capillary tubes are made by electrodeposition of a metal on a core, which is afterwards forcibly removed. The core may be Sn or like wire, which is melted and blown out from the deposit. Alternatively, a graphited thread, which may first have been waxed, or a steel or other refractory wire, preferably lubricated with graphite, may be used. A Cu cyanide or sulfate electrolyte may be employed throughout, or the two solns. may be used successively. With the cyanide soln., and a Sn wire, a current d. of 12-15 amperes per sq. ft. is suitable. The Cu tubes obtained may be 17-21 mm. long and of about 0.017 in. bore.

Electrodeposition of magnesium. G. O. SEWARD. Norw. 30,873, July 5, 1920. Mg is deposited by electrolyzing a melt of MgF_2 which contains MgO in such quantity that it does not completely dissolve in the melt, and which has a sp. gr. so high that the undissolved portion of the MgO cannot sink rapidly to the bottom.

Electrode mounting for boilers or condensers. A. S. GUSH. U. S. 1,366,257, Jan. 18. The pat. relates to electrodes employed for prevention of corrosion in steam boilers or condensers.

Electrode-holder for electric furnaces. C. W. HARPER. U. S. 1,366,073, Jan. 18.

Electric resistance material. L. McCULLOCH. U. S. 1,365,831, Jan. 11. An elec. resistance material adapted for use in rheostats is formed of a conducting material such as Ni steel having at least a portion of its surface coated with a material, *e. g.*, B_2O_3 and bentonite, which merely softens but does not melt on the application of heat.

Impregnating electrical condensers. P. THOMAS. U. S. 1,365,292, Jan. 11. Stacks of metal foil and paper or similar material for the formation of elec. condensers are immersed in a soln. of C_6H_6 and montan wax, removed from the soln. and immersed in a bath of commercially pure montan wax at a temp. of about 160° and then cold-pressed.

Electroplating with metals. B. BART. Can. 208,301, Feb. 8, 1921. An anode is prep'd. for electroplating by depositing metal upon a core composed of solid portions alternating with openings.

Electroplating and electrocleaning apparatus. ANDREW NESS. Can. 208,767, Feb. 22, 1921.

5—PHOTOGRAPHY

LOUIS DERR

Action of soluble iodides on the photographic plate. F. F. RENWICK. *Phot. J.* 61, 13-8(1921).—An exposed AgBr plate can be iodized, and a Ag image then developed after washing out all the sol. salts. A suitable iodizing bath is NaI or KI 10 g., Na_2SO_4 crystals 20 g., NaCNS or KCNS 30 g., water to 1 l. An amidol developer is used. It is noteworthy that hypo may be substituted for the thiocyanate, provided that white light is kept from the plate before development; the latent image is destroyed if white light falls upon the plate while the iodizing soln. is still in the film. This has led to a method of producing direct positives in the camera. An apparent fogging effect is produced by very dil. (1:20,000) solns. of KI applied for a few sec., but this is shown to be due to a marked color-sensitizing for yellow and red, no fogging occurring if the plate during or after bathing is not exposed to orange or red light. This seems to be the first recorded instance of color-sensitizing by bathing in a colorless bath. In concn. from 1:2000 to 1:1000 KCN has a similar effect.

L. DERR

Action of light on the photographic plate. G. I. HIGSON. *Phot. J.* 61, 35-44(1921).—The factors detg. the blackening of the AgBr gelatin plate are the photochem. law of the AgBr grain, the size or sizes of the grain, the diminution of light-intensity through the film, and the development. These are submitted to mathematical analysis, and the equations deduced lead to curves similar to the characteristic curves of plates as observed.

L. DERR

Halation preventives. H. LÜPPO-CRAMER. *Phot. Rundschau* 57, 326-30(1920).—A new German non-halation plate is coated with a gelatin substratum contg. finely divided and strongly light-absorbing MnO_2 , upon which the regular emulsion is coated. Acid-fixing baths of the usual character convert the MnO_2 into colorless salts easily removable by washing.

L. DERR

New methods for developing rapid and color-sensitive plates by candle-light. H. LÜPPO-CRAMER. *Phot. Rundschau* 57, 338, 367-8(1920).—Phenosafranine 1:2000 (Hoechst), applied 1 min. to an exposed plate before development, reduces its sensitiveness so much that development may be completed 1.5-2 min. from an ordinary lighted candle without fogging. Fixing must be thorough. Toluosafranine and brilliant

rhodulin red are also effective. Methylene blue is very active, but practically unavailable on account of its causing fog in all but the weakest concn. L. DERR

Toning developed prints by converting the image into colloidal silver. F. FORMSTECHEK. *Phot. Rundschau* 57, 8-10(1921).—The image is completely bleached in a bath of CuCl_2 30 g., HCl (1.17) 3 cc., $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 10 g., water 1 l. Hydrazine sulfate 1:50 gives blue tones, and yellow to red tones are given by ZnCl_2 10 g., HCl 1 cc., water 100 cc.; intermediate tones are given by 2% KNO_3 . Gaslight papers give better results than the more sensitive bromide papers. L. DERR

Departures from the reciprocity law. H. LÜPPO-CRAMER. *Phot. Korr.* 57, 168-9 (1920).—The general reaction is explainable by the hypothesis that the first illumination produces nuclei which by further exposure promote the disintegration of the AgBr at these points. L. DERR

A new photographic process without silver bromide. K. WILCKE. *Phot. Korr.* 57, 173-5(1920).—It is proposed to place a sheet of glass in the camera, covered with a thin layer of Se. Against this a sheet of thin, transparent paper is pressed contg. an electrolyte, and against this a metal plate. A transparent Au or Pt film placed between the Se layer and the glass, and connected with a source of electricity, causes local decompn. of the electrolyte in proportion to the light falling upon the particular spot, hence a picture is produced. L. DERR

Color photography. R. L. STINCHFIELD. U. S. 1,364,958, Jan. 11. A support such as glass or celluloid is provided with color-filter areas and non-filter areas of about the same size which may be arranged as parallel lines and is also provided with a sensitized coating which will yield an opaque image and with a light-reflecting surface behind the filter areas and image-forming coating. U. S. 1,364,959 relates to a similar arrangement of filter areas and sensitized coating on a photographic material.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

Preparation of thionyl fluoride and carbonyl fluoride. WILHELM STEINKOPF AND JULIUS HEROLD. *J. prakt. Chem.* 101, 79-81(1920).—The 2 methods given for making SOF_2 are suitable only for the prepn. of small quantities. Moissan and Lebeau obtained it by the action of SOCl_2 on AsF_3 (cf. *Compt. rend.* 131, 1436(1900), and Ruff and Thiel (*Ber.* 38, 549(1905)) from HF and N_2S_4 . The method of M. and L. has been now modified so that SOF_2 can be prepd. in much larger quantities. SOCl_2 is gradually added from a dropping funnel to the cooled AsF_3 in a flask connected with a Pb reflux condenser, the upper end of which is connected with a Pb receiver cooled to -50° to -60° . After the SOCl_2 has been added, the temp. of the mixt. is allowed to rise to room temp. and then gradually raised to 80° . Crude SOF_2 distils over while the higher boiling AsF_3 and SOCl_2 are returned to the flask. The product was purified by redistn. Its odor resembles that of SOCl_2 . In an analogous manner COF_2 was prepared from COCl_2 and AsF_3 . Since the reaction was not carried out in Pt vessels, but in Fe or glass, a pure compd. was not obtained, and the yield was small. The product prepd. solidified in liquid air and b. -160° to -150° . D. BREESE JONES

Note concerning the structure of some compounds. GERHARD KIRSCH. Uppsala. *Z. physik. Chem.* 96, 471-3(1920).—Kossel's idea regarding the relation between the chem. properties and the structures of substance (cf. *C. A.* 10, 2654) is discussed and applied to N_2 , CO , CN , O_3 (in ozone = O_3O), N_2O , NO , N_2 , and $-\text{CNO}$.

H. JERMAIN CREIGHTON

The constitution of paramolybdates. S. POSTERNAK. *Compt. rend.* 171, 1058-60 (1920).—P. discusses the constitution of the so-called paramolybdates and shows they are not distinctive in character from the ortho- and meta-molybdates, the difference being only in degree of hydration. He presents data showing the compn. of the mono-, tri-, and hexa-ammonium heptamolybdates, $\text{NH}_4\text{H}_2\text{O}_7\text{MoO}_4(\text{OH}) + \text{H}_2\text{O}$, $(\text{NH}_4)_3\text{O}_7\text{MoO}_4(\text{OH})$ and $3(\text{NH}_4)_2\text{O}_7\text{MoO}_4$, resp. S. A. BRALEY

The absorption of carbon monoxide by cuprous ammonium carbonate solutions. WM. R. HAINSWORTH AND E. Y. TITUS. *J. Am. Chem. Soc.* 43, 1-11 (1921).—Detns. have been made of the absorption of CO by 2 different $\text{Cu}_2(\text{NH}_4)_2\text{CO}_3$ solns. at different temps. and pressures. The absorption capacity of a soln. of a given Cu (ous) content depends on the content of free NH_3 and the partial pressure of the CO, as well as on the concn. of the Cu(ous). The absorption of the gas is due to the formation of an unstable compd. probably containing 1 mol. CO per g.-atom Cu(ous). The reduction of Cu(ous) to Cu takes place according to the equation: $\text{Cu}_2(\text{NH}_4)_2\text{CO}_3 + \text{CO} + 2\text{H}_2\text{O} - (2n - 4)\text{NH}_3 = 2(\text{NH}_4)_2\text{CO}_3 + 2\text{Cu}$, this reaction being comparatively slower than the corresponding reduction of Cu(ic) to Cu(ous): $2\text{Cu}_2(\text{NH}_4)_2\text{CO}_3 + \text{CO} + 2\text{H}_2\text{O} - (4 - 2n)\text{NH}_3 = \text{Cu}_2(\text{NH}_4)_2\text{CO}_3 + 2(\text{NH}_4)_2\text{CO}_3$. Used $\text{Cu}_2(\text{NH}_4)_2\text{CO}_3$ solns. can be regenerated by heating to 75° in an inert atm. H. J. CRRIGHTON

The influence of salts of the alkali and alkaline-earth metals on the solubility in water of calcium carbonate (a) in the presence of air free from carbon dioxide, (b) in the presence of excess of carbon dioxide. E. A. ROWE. *Trans. & Proc. New Zealand Inst.* 52, 192 (1920).—The app. used in the expts. is described. The soly. of CaCO_3 in H_2O increases regularly with additions of increasing small amts. of NH_4 , Na, K and Mg sulfates, NH_4 and Na nitrates, and NH_4 and Mg chlorides, but decreases regularly with the addition of increasing small amts. of NH_4 , Na and K carbonates, KNO_3 , KCl , and Na_2HPO_4 . The soly. of CaCO_3 in H_2O exhibits irregularities in the presence of small amts. of NaCl . The soly. of $\text{CaH}_2(\text{CO}_3)_2$ in H_2O increases regularly with the addition of increasing small quantities of NH_4 , Na, K and Mg sulfates; NH_4 , Na and K nitrates; NH_4 , Na, K and Mg chlorides; but decreases regularly with the addition of increasing small quantities of NH_4 , Na and K bicarbonates, CaCl_2 , and Na_2HPO_4 . As regards the alkalies, CaCO_3 appears to be more sol. in the NH_4 salt of a given acid, and in a sulfate of a given base. S. G. GORDON

The melting and boiling of ammonium sulfate. E. JANECKE. *Z. anorg. Chem.* 33, I, 278-80 (1920).—The melting and boiling of $(\text{NH}_4)_2\text{SO}_4$ were studied from the view-points of equil. of heterogeneous mixts. and the phase law. Tables and graphs are presented indicating that NH_4HSO_4 melts at 251° and boils at 490° , and that $(\text{NH}_4)_2\text{SO}_4$ does not possess definite transition points. Under atm. pressure a change in compn. of the neutral salt takes place at 357° , with the evolution of NH_3 and formation of a liquid residue. The salt melts and boils simultaneously. Theory indicates that at higher pressures definite transition points for both ammonium salts exist, but the conclusions have not been verified experimentally. W. C. EBAUGH

The ammonia-soda process. H. G. WILLIAMS. *Chem. News* 121, 295 (1920).—In the lecture expt. used to illustrate this process it was noticed that the ppt. obtained by passing CO_2 through concd. NH_4OH satd. with NaCl contained about 30% NaHCO_3 , 30% NaCl , the remainder being apparently NH_4HCO_3 . By treating with CO_2 a satd. soln. of NaCl subsequently satd. with NH_3 the ppt. contained about 92% NaHCO_3 . G. W. STRATTON

Organic salts of iron (BELLONI) 10. Synthesis of sulfuryl chloride in the presence of organic compounds (CUSMANO) 10.

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL.

Table of rays of great sensitiveness of the elements, for use in analytical research.

A. DE GRAMONT. *Compt. rend.* 171, 1106-9(1920).—A table includes most of the elements, giving the values in international Angström units of the wave lengths of greatest sensitiveness, derived from their spectra. Three sets of values are given, waves observed (1) by eye, and those from photography with (2) a crown glass and with (3) a quartz spectrograph. The rays were formed and measured by a method previously described (*C. A.* 8, 3268; 12, 1358).

C. C. DAVIS

Graphic representation of analytical results, particularly for water analysis.

CHARLES A. GRAU. Buenos Aires. *Ann. chim. anal. chim. appl.* 2, 358-9(1920).—This is an application of the hexagon of Marion (*C. A.* 14, 2828) to the classification of natural waters. It has been described previously (*Revue physis, Buenos Ayres*, III, 454(1917); *Annales de la société chimique argentine*, VI, 102(1918); *Annales de la société de physique et chimie, Madrid*, XV, 477(1918); *Mémoires de l'académie royale des sciences et arts Barcelona*, XV, 10(1919)).

C. C. DAVIS

Standardization of laboratory methods. AUGUSTUS B. WADSWORTH. N. Y.

Dept. of Health. *Am. J. Pub. Health* 10, 932(1920).—The necessity for uniform methods is pointed out and the extent to which Government supervision has been attempted in Germany, France, England and the U. S. A. is indicated. W. T. H.

The detection of hydrochloric acid in the presence of hydrobromic and hydriodic acids. G. G. LONGINESCU AND GABRIELA CHABORSKI. Univ. Bucharest. *Bull. sec. sci. acad. Roumaine* 6, No. 5-6 rep. (1919-20).—In the following method the HBr is eliminated by means of ethylene formed from alc. and H_2SO_4 . *Procedure.* Place a little of the solid substance in a dry test-tube and add 3 cc. of a mixt. of 2 parts of alc. and 1 part of concd. H_2SO_4 . Place over the test-tube an inverted funnel containing a filter paper moistened with 5% $AgNO_3$ soln. Heat the test-tube until the heat of the evolved vapors just makes it impossible to hold the tube in the hand, and then remove the flame. The HCl is evolved and is retained on the filter paper as AgCl. The HBr is partly decompd. into Br_2 and H_2 . The Br_2 and undecomposed HBr are absorbed quant. by the liquid mixt. forming C_2H_5Br and $C_2H_4Br_2$. Some C_2H_5Br vapors may escape, but they do not react with the $AgNO_3$ on the filter paper. If HI is present it is decomposed almost completely. Most of the I_2 remains in the soln., but a little escapes and forms AgI on the filter paper. The filter paper is washed, while in the funnel, with 2-3 cc. NH_4OH , and the resulting filtrate is acidified with HNO_3 . A white ppt. indicates the presence of HCl. The presence of HI is shown by violet vapors of I_2 which are evolved during the heating, and by a yellow ppt. of AgI, insol. in NH_4OH , which forms upon the filter paper. To test for HBr, heat the mixt. which remains in the test-tube hotter than before, and ignite at the mouth of the tube the vapors of C_2H_5Br and $C_2H_4Br_2$ which are evolved. Invert over the flame a beaker whose walls have been moistened with H_2O . The HBr, HI and I_2 from the flame are dissolved on the wet walls of the beaker. Rinse the walls of the beaker and transfer the soln. to a test-tube. Add to this soln. a little CS_2 , and then some dil. Cl_2 -water drop by drop, until the violet color of the I_2 disappears. A brown or yellow color of the CS_2 indicates the presence of HBr. In the presence of HNO_3 the Br_2 is not completely absorbed by the ethylene, and partly escapes. This may be avoided by using, for the formation of the ethylene, a mixt. of 2 parts of alc. and 1 part of a H_2SO_4 soln. of diphenylamine. R. H. L.

Micro-reactions of the iodate ion. G. DENIGES. *Bull. soc. pharm. Bordeaux* 58, 211-14(1920).—A reagent for the microchem. identification of the IO_3^- ion is prepd. by dissolving 1 g. of $TiOAc$ in 20 cc. of H_2O . The test is carried out by placing a drop of the soln. to be tested and a drop of the reagent on a glass slide and bringing the two

in contact laterally by means of a Pt wire or a glass filament. In HIO_3 concns. of 1 g. per l., or greater, the crystals of TiIO_3 form in groups. When a diln. of 0.3 to 0.2 g. per l. is approached, these groups are transformed into small octahedrons with a square base, some of them occurring in groups of four resembling sarcines. To detect the IO_3^- ion in Chili saltpetre, dissolve 5 g. of the latter in 10 cc. of H_2O . If a drop of this soln. is treated with a drop of the TIOAc reagent, typical groups of crystals are obtained when the IO_3 ion is present in the nitrate to the extent of 1 part in 250, and the octahedrons down to 1 part in 1000.

A. G. DuMEZ

Microchemical reactions of iodic acid. A. BOLLAND. *Compt. rend.* 171, 955-7 (1920).—(a) TiNO_3 . In the first phase of the reaction needles are formed which appear white macroscopically, but black microscopically. In the second phase, these needles unite to form crosses or filiform crystals; av. size 40μ ; admissible diln. 1:5000. (b) AgNO_3 . The product of the reaction is amorphous. After dissolving in NH_4OH and evapp. the solvent, colorless rhombic tablets are obtained; these unite to form dark colored groups of a size up to 100μ ; admissible diln. 1:5000. (c) BaCl_2 ppts. straight or curved needles; generally united in bundles in groups of 2 or 4. Size up to 300μ ; admissible diln. 1:2500. (d) $(\text{AcO})_2\text{Sr}$ gives needles and slender prisms grouped in balls or combined in parallel bundles, often in the form of crosses; size up to 100μ . Conc'd. solns. give large X- or horn-shaped crystals (up to 150μ); small crystals colorless; conglomerates appear dark. Admissible diln. 1:300. (e) $(\text{AcO})_2\text{Ca}$ gives colorless octahedra. The extinction between crossed nicols indicates that they are of the monoclinic system. They may appear singly or grouped in stars. Conc'd. solns. yield first an amorphous ppt., which becomes rapidly crystalline. Av. size 150μ ; admissible diln. 1:300. (f) RbCl gives rectangular tablets, often truncated so as to appear as pentagons or hexagons. These tablets are colorless, strongly refractive, and remain dark between crossed nicols. Av. size 25μ ; admissible diln. 1:300. (g) CaSO_4 gives different crystalline forms; colorless and, strongly refractive; the most characteristic are hexagonal or octagonal lamellae. Av. size $50-80\mu$; admissible diln. 1:80. (h) KCl gives colorless hexagonal tablets or prisms, often united, and between crossed nicols appearing as anisotropic crystals. The prisms have an av. length of 80μ and width of 50μ . Admissible diln. 1:60. (i) AcONa yields octahedra, prisms and combinations of the 2 forms. The prisms are often united in filiform crystals; av. size 25μ , admissible diln. 1:60. (j) Conc'd. NH_4OH ppts. colorless rectangular tablets, often combined in bi-refrinct filiform crystals. Av. size 40μ ; admissible diln. 1:35. (k) MnCl_2 yields aggregates composed of a large no. of needles, which polarize between crossed nicols. Under the microscope these aggregates appear of a grayish green color (macroscopically white); av. size 25μ ; admissible diln. 1:20. The reactions with CdCl_2 and ZnSO_4 are not applicable owing to the formation of amorphous ppts. F. W. S.

General method for the detection and determination of arsenic. KOHN-ABRESCH. *Compt. rend.* 171, 1179-82 (1920).—The procedure is for use in exptl. medicine. Org. material is incinerated with a mixt. of MgO and $\text{Mg}(\text{NO}_3)_2$ instead of the older method of MgO with excess HNO_3 . Add to 100 g. of ground material 35 cc. of $\text{Mg}(\text{NO}_3)_2$ soln. (200 g. per l.) and 1 g. of MgO . Dil. and heat at 250° to carbonize all org. material. Pulverize the residue and heat at 500° until free of C. Dissolve in 30 cc. 10% H_2SO_4 and test for As by the Marsh method. 0.00003 part As per 100 of viscera can be detected. To det. As in org. As compds. add 0.2 g. of MgO and 6 cc. of $\text{Mg}(\text{NO}_3)_2$ soln. to 0.15-0.20 g. of unknown. Heat at 110° until dry. Cover and heat to redness until decompd. Dissolve in HCl and det. Cf. Fleury C. A. 14, 2600. C. C. DAVIS

Estimation of sulfur by the lamp method. F. ESLING. *Chem. Age (London)* 3, 684-5 (1920).—A weighed amt. of oil, either by itself or dissolved in a suitable solvent, is burned in a lamp, the products of combustion are passed into a measured vol. of

standard Na_2CO_3 soln. and the excess of alkali is detd. by titration with standard acid.

W. T. H.

The qualitative and quantitative determination of nickel and cobalt. MOROOKI MATSUI AND TADASU NAKAZAWA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 4, 265-71 (1920).—The dimethylglyoxime test for Ni can be applied to a mixture of hydroxides by simply adding the reagent without dissolving the hydroxides. If a mixture of Ni and Co is treated with dimethylglyoxime in the usual manner and the Ni ppt. removed, Co in the filtrate may be detected by adding a drop or two of $(\text{NH}_4)_2\text{S}_2\text{O}_8$; a trace of Co suffices to give a red coloration. The Ni salt of dimethylglyoxime can be dissolved in NaOH soln. and the Ni deposited electrolytically. Similarly, after pptg. the Ni with glyoxime, the Co in the filtrate can be detd. by adding caustic alkali and electrolyzing. Instead of caustic soda, ammonia and $(\text{NH}_4)_2\text{SO}_4$ may be used.

W. T. H.

The determination of bismuth by means of thiourea. ANT. JILRK. *Chem. Listy* 14, 165-6 (1920).—Bi in HNO_3 soln. in the presence of low concns. of Cl^- , SO_4^{--} , and PO_4^{--} anions and Ag, Pb, Hg^+ , Cu, Hg^{++} , As, Sb, Sn, Al, Zn, Mn, Ca, Sr, Ba, Mg, NH_4 , K, Na cations, can be easily detd. by means of a 15% soln. of thiourea with which the Bi forms an intense yellow coloration. If Hg^+ is present a grayish ppt. is first formed, which must be filtered off. If colored cations such as Fe^{+++} , Ni^{+++} , Co^{++} , and Cr^{+++} are present in considerable quantities, it is best to ppt. first with H_2S , then dissolve the sulfides in (1:1) HNO_3 , heat and filter off any S formed. The Bi is then detd. in the filtrate.

JOHN M. KRNO

Estimation of arsenic in organic compounds. GEORGE ROSS ROBERTSON. *J. Am. Chem. Soc.* 43, 182-5 (1921).—After reviewing the more convenient methods for this work a method is described which can be carried out in 2 hrs. with little attention. The sample is oxidized with HNO_3 and H_2SO_4 , freed from nitrous compds. by treatment with $(\text{NH}_4)_2\text{SO}_4$, reduced with HI and the AsO_2^- titrated with standard I_2 in the presence of Na_2CO_3 .

C. A. ROUVILLER

The catalytic decomposition of alkaline sodium hypobromite solution by copper sulfate. Antagonistic action of iodine. P. FLEURY. *Compt. rend.* 171, 957-60 (1920).—F. reports expts. showing the decompn. of alk. NaBrO solns. by CuSO_4 and points out the significance of small amts. of Cu (impurity) in the NaOH used in the prepn. of solns. for detg. small amts. of *urea*. The rate of decompn. increases rapidly with the concn. of the Cu salt (1 part of Cu in 100,000 causes the decompn. of 42% of the NaBrO in 24 hrs. at 36-37°). The addition of 1 part in 1000 KI or KIO_3 inhibits the evolution of O without influencing the transformation of NaBrO to NaBrO₂.

F. W. SMITHER

Experiences of a custom assayer. E. C. D. MARRIAGE. *Eng. Mining J.* 110, 906 (1920).—An account of experiences with salted samples.

F. W. SMITHER

Separation and detection of lactic acid as complex sodium ferric lactate. K. A. HOFMANN. *Ber.* 53, 2224-6 (1920).—The salt is practically insol. in water and is formed as a pale-green ppt. by digesting a dil. soln. of lactic acid with FeCl_3 for some time. The Fe is present in a complex anion. By shaking with water, a pale-yellow suspensoid is obtained of neutral reaction. Dil. NH_3 soln. attacks the ppt. exceedingly slowly and 15% AcOH has practically no effect upon it. Stronger acids dissolve it and stronger bases decompose it, forming the hydroxide. To detect ordinary lactic acid with the aid of this salt, add a slight excess of FeCl_3 , make distinctly alkaline with Na_2CO_3 and then add AcOH until acid. Concentrate the soln. on the water bath and after a few hrs. the ppt. will form, even when only a little lactic acid is present.

W. T. H.

Iodometric determination of amino nitrogen in organic substances. H. H. WILLARD AND W. E. CAKE. *J. Am. Chem. Soc.* 42, 2646-50 (1920).—The Kjeldahl method is made more rapid by adding $\text{K}_2\text{S}_2\text{O}_8$ to the charred soln. of org. matter in H_2SO_4 . The NH_4 salt is detd. by adding an excess of standard NaBrO soln., causing the excess of

the latter to react with KI in acid soln. and titrating the liberated I_2 with $Na_2S_2O_4$.

CHAS. A. ROULLER

A new method for the estimation of histidine. W. E. THRUN AND P. F. TROWBRIDGE. Agr. Expt. Sta., Columbia, Mo. *J. Assoc. Off. Agr. Chem.* 4, 194-5(1920).—Bromination of the soln. of the bases of a coagulable protein sample indicates that it is possible to det. histidine without using the Van Slyke app. H. A. LEPPER

The mechanism of some combustions. H. V. WARTENBERG AND B. SIEG. *Ber.* 53, 2192-2202(1920).—Gas explosion expts. were performed with CO , H_2 , $(CN)_2$ and CH_4 in support of the theory that the primary products are unstable addition compds. When CO reacts with O_2 in the presence of moisture, formic acid is formed from CO and H_2O and this acid breaks down into CO_2 and H_2 . The H_2 forms H_2O_2 with O_2 and the H_2O_2 breaks down into H_2O and O_2 with the formation of some O_3 (cf. Dixon, *J. Chem. Soc.* 49, 94(1886)). The combustion of cyanogen apparently gives rise to a primary oxidation product of a peroxide nature. With CH_4 , formaldehyde and water are the primary products (cf. Bone and Wheeler, *C. A.* 2, 1526) and from these CO and CO_2 result. W. T. H.

New indicator (KINKAD) 10.

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

New mineral species described during 1916-1920. EDGAR T. WHERRY. Wash., D. C. *Am. Mineral.* 6, 12-7(1921).—About 75 minerals are listed, with their formulas and a critical discussion of their status. They are arranged in 9 families, starting with native elements and ending with the most complex silicates, the order of Dana being departed from toward the end. About 1/3 of them are so inadequately established that they are included in a "doubtful and discredited" section. This suggests the need for more thorough study of minerals, especially as to their optical properties, which are regarded as best for the establishment of species, before they are announced as new.

E. T. W.

A new classification of the sulfo-salt minerals. EDGAR T. WHERRY AND WILLIAM F. FOSHAG. *J. Wash. Acad. Sci.* 11, 1-8(1921); cf. *C. A.* 15, 40.—The sulfo-salt minerals have been assigned to divisions, based on the ratios of basic and acidic sulfides, and to groups based on crystn. Minerals containing both univalent and bivalent metals have been classed as double compds. rather than as isomorphous mixtures, a number of evident admixtures having been thrown out before calculating formulas from analyses. A higher S content in some cases has been interpreted as due to a higher state of oxidation of the metal rather than the non-metal, resulting in the discarding of the "sulfarsenate-sulfantimonate" division. About 75 sulfo-salt minerals are listed in an annotated table with their formulas. S. G. GORDON

Cleavable bornite from Usk. B. C. T. L. WALKER. Univ. Toronto. *Am. Mineral.* 6, 3-4(1921).—A bornite showing unusually perfect octahedral cleavage was examd. mineragraphically by E. Thomson. It was found that chalcocite was present in large amts. Analysis by A. C. Wheatley showed a compn. corresponding to $7Cu \cdot S \cdot FeS_2$, a formula shown also by an older analysis of material from Ragisvaara. The B.C. mineral being proved to be a mixture, however, the other is probably the same. It is a mere chance that the 2 indicate a simple ratio; and it is plainly unsafe to use occurrence of material of the same compn. at 2 widely sepd. localities as a criterion of its definite character, for both may be mixtures. The exact formula of the bornite present cannot be decided. The mineragraphic relations indicate the mixture to be a partial alteration of bornite to chalcocite. E. T. W.

Cristobalite in the spherulitic obsidian from Yellowstone National Park. AUSTIN F. ROGERS. Stanford Univ. *Am. Mineral.* 6, 4-6(1921).—The n of the obsidian is 1.480, which proves that it is rhyolitic, and high in SiO_2 . In the lithophysae are rods of orthoclase, with $n = 1.523$, and cristobalite, in minute spherical aggregates. It is readily identified by its n , 1.485, and by its behavior on heating and then cooling, when it becomes opaque suddenly at a transition point around 200° . Since cristobalite is a form of SiO_2 , it would be expected to occur mostly in persilicic rocks, although the earlier described occurrences were in subsilicic rocks. That it is also characteristic of the former type of rocks is shown by the present and other recently described American occurrences (C. A. 12, 1034).

E. T. W.

Massive laumontite from Montana. EARL V. SHANNON. U. S. Nat. Mus. *Am. Mineral.* 6, 6-7(1921).—A massive mineral was found by E. S. Larsen to be optically —, with $\alpha = 1.505$, $\beta = 1.515$, $\gamma = 1.517$, agreeing with laumontite, which is, however, usually cryst. and very different in appearance and properties. Analysis by S. showed that it has, in fact, the compn. of laumontite, thus indicating how certainly a mineral can be identified by its optical properties alone.

E. T. W.

The minerals of Madison County, Missouri. W. A. TARR. Univ. Mo. *Am. Mineral.* 6, 7-10(1921).—The occurrences and relations of the minerals are described. The rare mineral *bieberite*, $\text{CoSO}_4 + 7\text{H}_2\text{O}$, is reported as an alteration product of the linneite, $(\text{Co,Ni})_2\text{S}_4$.

E. T. W.

Platinum in meteoric irons: A correction. GEORGE P. MERRILL. *J. Wash. Acad. Sci.* 10, 597(1920).—Pt has become one of the well recognized constituents of meteorites, and has been detected in the Yenberrie, Barriata, Cowra, Delgate, Gilgoir, Molong, and Mount Dyrirring irons.

S. G. GORDON

Chemical and mineralogical work. EDWARD S. SIMPSON. *Ann. Progr. Rept. Geol. Survey for the year 1919, Western Australia*, 34-41(1920).—*Alunite* from Kanowna, Wallangie, Northampton and Ravensthorpe ran from 5.0% to 10.8% K_2O for the clean mineral. An industry is established at Kanowna. To each ton of alunite 200 lbs. or more dry slaked CaO are added and the mixt. is applied to the surface of the soil or covered in to a shallow depth. The CaO treatment saves the cost of roasting, but adds to the wt., reducing the grade in K_2O by 10%. The K_2O becomes water-sol. by this addition. The av. of 13 samples of *glass sand* from Lake Gnangara was SiO_2 , 99.72 and Fe_2O_3 , 0.039%; of 2 samples from Cannington, SiO_2 , 99.53 and Fe_2O_3 , 0.046%. The proportions of NaCl in the waters of a number of lakes which form *salt* deposits during the dry season are given. The quality of crude salt obtained from various lagoons and lakes ranged from 93.56 to 99.90% NaCl . A sample of *ceylonite* from Namban analyzed: MgO 13.65, FeO 17.45, MnO 0.26, Fe_2O_3 3.80, Al_2O_3 42.09, Cr_2O_3 22.76%, H_2O and SiO_2 , nil. Analyses of 13 samples of *Fe ore* from Clackline and Yampi Sound and of 6 samples of *gypsum* are reported. A sample of *iolite* from Westonia ran SiO_2 45.10, Al_2O_3 29.57, Fe_2O_3 0.24, FeO 4.26, MnO 0.38, MgO 9.56, CaO 1.06, Na_2O 1.27, K_2O 4.28, H_2O 4.42%, TiO_2 , nil. Analyses are also reported of 2 samples of *emery*, 3 of *magnesite* and 1 of *psilomelane*.

ALBERT R. MEREZ

Magnetite deposits of the Eastern Mesabi Range, Minn. FRANK F. GROUT AND T. M. BRODERICK. Minnesota Geol. Survey, *Bull.* 17, 54 pp.; *Eng. Mining J.* 110, 373(1920).—G. and B. describe the eastern end of the Mesabi Range where the Fe-bearing formation has been metamorphosed by the intrusive Keweenawan gabbro, changing the Fe into magnetite. Amphibole is abundant and pyroxene, fayalite and garnet occur as metamorphic minerals, the amphibole probably resulting from alteration of the glauconitic mineral greenalite. The metamorphism has not changed the distribution of Fe. The derivation of the ores in the beds previous to the metamorphism is discussed, the conclusions being similar to those of previous students of the area with, however, some original variations.

E. V. SHANNON

Further notes on the gold deposits of the Southern Appalachians. JAMES FRAMER. *Eng. Mining J.* 111, 4(1921).—Gold occurs in a belt from Va. to Ala., reaching its greatest development at Dahlonega, Lumpkin Co., Ga. The enclosing rocks are hornblende gneiss. The deposits are of 4 classes: (1) placers; (2) free-milling quartz veins; (3) non-free milling veins, and (4) mineralized zones in schists. Outcrops are rare owing to surface decompn. The Au averages 990 fine. The free-milling veins are small, irregular and free from sulfides, except galena, which is an indicator of Au. The sulfide veins are wider and of more uniform value. The mineralized zones in schist vary up to 18 ft. in width and sometimes carry pockets of coarse Au. E. V. S.

Ore deposits of the Cave Creek Dist., in Arizona. ALFRED S. LEWIS. *Eng. Mining J.* 110, 713-6(1920).—L. describes the geology of the district which is in Maricopa Co., 28 miles north of Phoenix. The Red Rover, the only important mine, has a deposit of highly argentiferous Cu ore in schist. Other occurrences of Cu minerals in the district are discussed. E. V. SHANNON

Copper ores of Lake Superior. J. E. SPURR. *Eng. Mining J.* 110, 355-7(1920).—The general features of the region are briefly summarized with a compact description of the ores. Attention is directed to small veins containing chalcocite, bornite and chalcopyrite and also domeykite, smallite-chloanthite, etc. S. believes that the ores were deposited at great depth by magmatic solns. rich in Cu and deficient in S, etc., containing some Ag, Co, Ni, etc. Ore deposition was accompanied by very little alteration of the enclosing rocks. Theories of origin by ground water are shown to be inapplicable. The source of the material of the ores was probably some one of the granite intrusions near the base of the Keewenawan series. The ore-depositing solns. gained access through channels rendered permeable by strain preceding the formation of the Keewenaw fault, which limits the ore-bearing zone on the east and which is not mineralized. E. V. SHANNON

Platinum in Colombia. J. OVALLE. *Eng. Mining J.* 110, 907-8(1920).—O. gives figures on recent production and prices for Pt. Colombia is second only to Russia in production. The location and distribution of the important deposits are given. The Pt occurs with Au in alluvial deposits. Independent native miners are being replaced by English and American companies employing steam dredges. The Colombian and Urals fields are compared as regards past and present production and future outlook. E. V. SHANNON

Tin and tungsten deposits—economic significance of their relative temperatures of formation. C. G. CULLIS, et al. *Bull. Inst. Mining Met.* 1920, Nos. 187 and 188; discussion of C. A. 14, 3622.—Evidence of various Sn-mining regions is cited to show that cassiterite is essentially a higher-temp. mineral than is wolframite, pure wolframite veins passing in depth into wolframite-cassiterite veins and deeper still into wolframite-free cassiterite veins. This is thought to have an economic bearing as cassiterite veins cannot be expected to contain more wolframite with depth, while wolframite veins in a Sn-bearing region may give way to ore richer in Sn at greater depth. The discussion suggests extending the theory to cover deposits of other metals, and also points out certain exceptions to the general rule. C. G. CULLIS: The rule is not applicable to some Bolivian deposits when in the absence of sufficient B and F, Sn was expelled in part as sulfide which remained in soln. at lower temps. and was carried up into the hydrothermal zone and deposited with Cu and Fe as stannite. The stannite by oxidation gives secondary deposits of cassiterite. Contact metamorphic and metasomatic Sn and W deposits are discussed, also transition of pegmatite into quartz veins and the chemistry of Sn and W fluorides. E. V. SHANNON

Molybdenite; its occurrence, detection and determination in partly oxidized molybdenite ores. J. P. BONARDI. *Chem. Met. Eng.* 23, 205-6(1920).—Molybdenite, which occurs as an alteration product of Mo ores, is not recoverable by ordinary concn. proc-

esses and is lost. The deposit at Climax, Colo., the largest in the U. S., contains from 10 to 20% of the Mo in this form. This can be partly recovered by sulfidizing flotation using Na_2S , but MoO_3 is sol. in alk. sulfides so that the soln. must be kept nearly neutral for efficient recovery. The Mo can be recovered from the alk. soln. by adding CaCl_2 and boiling. Molybdenite occurs usually near the outcrops of Mo veins and disappears at slight depth. At Climax it occurs throughout the known orebody, being abundant at 350 ft. below the surface. Qual. tests for detection of molybdenite are as follows: Digest the finely ground ore with 200 cc. of 10% soln. of HCl , Na_2CO_3 , or NH_4OH in an Erlenmeyer flask, boiling 30 min. The soln. is then filtered. If HCl was used the soln. is made ammoniacal before filtering. The filtrate is acidified with HCl and some H_2O_2 added; it is then boiled to destroy H_2O_2 , and made ammoniacal. Any ppt. is filtered out, the soln. acidified and some alkali thiocyanate is added, followed by Zn. Mo gives a cherry-red color which is extd. by ether. A quant. method is given, using similar extn. methods, the Mo being weighed as PbMoO_4 . E. V. SHANNON

Wombah molybdenite mine and mill, Queensland, Australia. J. H. REID. *Eng. Mining J.* 110, 947 (1920).—The mine is probably the most important Mo mine in Australia. The ore occurs in a quartz pipe in granite near a granite-porphry dike and near the contact of granite and slates. Some calcite, chalcopyrite, pyrite, galena and blende occur with the molybdenite. The ore is richest around the edge of the deposit. The mill feed averages 0.8% MoS_2 . The best ore is hand picked, the balance being milled by flotation. Production in 1919 was 41 long tons of 90% MoS_2 concentrates. E. V. SHANNON

Tungsten ore deposits in Burma. J. COGGIN BROWN. *J. Soc. Chem. Ind.* 39, 44-8T (1920); cf. *C. A.* 14, 1280.—W ores have been known to occur in Burma since 1846 or earlier. The deposits of Tavoy were rediscovered in 1909. Burma held first place as a producer of W from 1911 to 1916 when it was surpassed by the U. S. and Bolivia. Up to 1913 Germany held control of 2/3 of the world's production of W by handling concentrates and the beginning of the war found Great Britain with almost no reserves. The British Govt. assisted mining and the production of Burma rose from 1888 tons in 1913 to 4480 tons in 1917. During the war Burma exported 17,636 tons of concentrates valued at 2,322,000 £. Wolframite occurs with cassiterite over a length of 750 miles. The Tavoy Region, which is the most important, is in S. Burma. Tin and W ores occur in and near the margins of white siliceous granite intrusions in clay slates. The ores occur in segregations in the granite, in pegmatites, and in quartz veins in both intrusive and intruded rocks. Other minerals occurring in the ores are mica, fluorite, molybdenite, pyrite, chalcopyrite, arsenopyrite, galena, spalerite, Bi, bismuthinite, and topaz. Statements that columbite and tourmaline occur are erroneous. Sn and W occur in bands of altered granite (greisen) adjoining the veins and in residual detrital and talus deposits on slopes. The veins are classified and their distribution is discussed. The sequence of deposition was molybdenite-wolframite-cassiterite. The ratios of Sn to W vary. W ores are rapidly disintegrated and destroyed by weathering and consequently do not concentrate in the gravels. A bibliography is given. E. V. S.

Economic minerals of Madagascar. GEORGE F. KUNZ. *Eng. Mining J.* 111, 14-6 (1921).—An article compiled from an address by A. Lacroix at the French Natl. Museum of Nat. History, Paris, May 2, 1920, and an article by Duparc on minerals of the pegmatites, published in Geneva in 1910. Notes are given on graphite, corundum and rare earths. The graphite occurs in crystalline schists which have been converted to lateritic deposits. Corundum of abrasive quality is extensively mined. The rare earth ores include rutile, titanite, autunite, fergusonite, samarskite, euxenite; also the minerals peculiar to Madagascar, betafite, samiresite, blomstrandite and ampangabeite. These are easily mined as they occur in much decomposed alkali pegmatites. One deposit has produced 20 tons of betafite. These minerals are hard to market as U

ores, because of complexity of treatment and because of the presence of Th. Large crystals of monazite occur and also large deposits of zircon. Gem minerals include beryl of various colors, tourmaline and garnet.

E. V. SHANNON

Pyrite in the Huelva District, Spain. COURTNEY DE KALB. *Mining Sci. Press* 122, 125-30(1921).—The production for 1918 was about one and a half million metric tons, of which the Rio Tinto Mine produced the greater part. Large tonnages of ore are stored in leach-piles on the surface. The copper is perfectly extd. and the S content of the residual pyrite thus raised. This operation takes about ten years, at a very low cost, fully 80% of the copper having been extracted during this period. The estd. reserves for the Rio Tinto Mine are 56,000,000 tons, and 230,000,000 tons for the district. The ores as mined average 2% Cu and 45% Fe. The orebodies conform to the direction of numerous diabase dikes, and are commonly associated with them. A. H. HELLER

Interrelations of fossil fuels. IV. JOHN J. STEVENSON. *Proc. Am. Phil. Soc.* 59, 405-511(1920); cf. *C. A.* 10, 1832; 11, 2183; 12, 892.—A detailed review of the stratigraphy, paleontology and paleobotany of the Permo-Carboniferous coals of Australia, India, Siberia, European Russia, Spitzbergen, Silesia, Hungary, Bohemia, Germany, Belgium, northern France, Spain, Great Britain and South America. W. B. V.

Additional facts concerning the distribution of igneous rocks in New Zealand. II. J. A. BARTRUM. *Trans. and Proc. New Zealand Inst.* 52, 416-22(1920).—The following rocks are described: quartz-norite from Cleddau-Hollyford Saddle, Otago, with an analysis; norite from Wairau Creek, Milford, Auckland; dolerite from Swinging-Basin, Silverdale, Auckland; basalt from "Sugarloaf," Rodney County, Ti Point, Rodney County, and Ohakune; and hypersthene andesite from Mount Hikurangi. An undetermined pyroxene resembling hypersthene occurs in the quartz-norite, but is monoclinic, and probably represents a monoclinic member of a series including hypersthene.

S. G. GORDON

Geological memoranda. WALTER HOWCHIN. *Trans. and Proc. Royal Soc. N. South Wales* 43, 45-58(1919).—Occurrences of "sarcen" stones in South Australia, and pumice, scoriaceous lava, torbanite, asphaltum, and fossil resin in the sea-drift near Cape Banks, are described. Opal deposits occur in the upper portions of the Cretaceous clays of South Australia, forming thin reticulated veins or cylindrical bodies. A fair-sized opalized tree was brought to Adelaide, but in a short time the specimen cracked to pieces. On examn. it was found that an efflorescence of salt covered all the planes of fracture, the crystn. of which from soln. caused the cracking. Salt is thus an active agent causing the mechanical disintegration of rocks in arid regions. Nodular barite of peculiar form occurs in Australia, believed by H. to be the result of the filling of cavities formerly occupied by annelids; 2 analyses of the *barite* are given. S. G. G.

The conglomerate at Albany, Lucas Creek, Waitemata Harbour. J. A. BARTRUM. *Trans. and Proc. New Zealand Inst.* 52, 422-30(1920).—A conglomerate is described consisting of pebbles and boulders up to 1.5 ft. in diam., 90% of which were of igneous origin. Petrographic descriptions of the rocks recognized are given. S. G. G.

A geological reconnaissance in the southern portion of the Yalgoo gold field. H. W. B. TALBOT. *Annual Progress Report of the Geological Survey for the year 1919, Western Australia*, 7-12(1920).—A metamorphosed schist, probably of sedimentary origin, designated as a chloritic quartz-cyanite rock, analyzed: SiO_2 72.57, Al_2O_3 10.15, Fe_2O_3 0.49, FeO 2.70, MnO 0.05, MgO 9.38, CaO nil, K_2O 0.28, Na_2O 0.34, H_2O +3.19, H_2O -0.02, TiO_2 0.57, and P_2O_5 0.20%.

ALBERT R. MERE

A New Zealand department of volcano research. T. A. JAGGAR. *New Zealand J. Sci. Tech.* 3, 162-7(1920).—The object, equipment and cost of volcanic research are described, with a summary of the results achieved at the Hawaiian observatory.

S. G. GORDON

Measurement of the density of minerals (ADAMS) 1. Influence of salts of the alkali and alkaline-earth metals on the solubility in water of calcium carbonate (ROWE) 6. Acidity of Japanese acid clay (KOBAYASHI) 15.

9—METALLURGY AND METALLOGRAPHY

WILLIAM BRADY, ROBERT S. WILLIAMS

Milling and flotation processes. THOMAS VARLEY. *Salt Lake Min. Rev.* 22, No. 5, 37-8(1920).—V. gives factors that must be known for detg. the particular processes for various ores. Various types of ores are described, and descriptions given of gravity concn. and of straight and differential flotation processes. Both the Horwood and wet methods of differential flotation are dealt with. A. H. HELLER

Lead salts in the cyanidation of silver ores. RALPH W. PERRY. *Min. Sci. Press* 122, 221-5(1921).—An increase in extn. of Ag ores by cyanidation is obtained when Pb salts are used, which is explained in part by the fact that Pb salts ppt. sol. sulfides from the solns. as insol. PbS, thus preventing the repptn. of the Ag already dissolved. Sulfides of Sn, As, Cu, Zn, Sb, Ni, Fe, Mn and Bi ppt. Ag from cyanide solns., the % of pptn. decreasing from as high as 90% with SnS_2 to no pptn. with Bi_2S_3 . If Pb salts are added the Pb will be pptd. by the above sulfides in preference to the Ag, the PbS formed being inert towards Ag. If Zn is present in soln. it would be pptd. by the sulfides, and the ZnS would in turn ppt. Ag. If Pb salts are present they will be pptd. in preference to the Zn. The amt. of Pb salts required is very small, since only a film of PbS upon the sulfides is all that is required to destroy their pptg. power. A. H. H.

Roasting furnaces for sulfide ores. H. M. RIDGE. *Chem. Age (London)* 3, 586-7(1920).—An historical review of the subject of roasting of pyritic ores.

H. L. OLIN

Metallurgical methods at Rio Tinto. COURTNEY DE KALB. *Min. Sci. Press* 122, 185-91(1921).—Only 1.6% of Welsh anthracite coal is required in the blast furnaces. A 20% mat is produced which is converted to 98.5% Cu. The cementation plant contains 18 1/2 million tons of ore in 3 heaps. Leaching is accomplished by oxidation of the Cu sulfides in the presence of moisture, pyrite being attacked only to a small extent even after 20 years, the total shrinkage being less than 7%. Successful operation depends upon proper ventilation. The S content of the ore is raised from 46% before to 49% after leaching. About 86% of the Cu is extd. after 3 to 3 1/2 yrs., and reaches a total of 95% after 15 to 20 yrs., the coarser material yielding up its Cu more readily than the fines. The soln. in the pptg. vats contains 20 g. Fe, 3.4 g. Cu, 2 g. Zn, and 8.5 g. H_2SO_4 per l. The Cu is pptd. on pig or scrap iron, and the spent soln. is pumped back to the leach piles. The ppt. averages 70% Cu and is concd. to a 90% product. 1 1/2-2 1/2 parts of Fe are consumed per part of Cu pptd. A. H. H.

Converting high-grade mat in magnesite-lined converters. H. C. ROBSON. *Bull. Inst. Mining Met.*, 1920, No. 194, 10 pp.—Blowing of mats of 60% Cu and over was practiced by the Spassky Copper Mine, Ltd., Akmolinsk, Siberia, using small Great-Falls type basic converters. The charge was blown so as to keep a protective coat of Fe_2O_3 on the brick lining. The converters ran for 3 years without repairs to lining except at the tuyères, where there was abrasion by large lumps of secondary material which was charged cold. One of the chief difficulties in blowing high mats is in keeping the tuyères open; this was overcome by keeping the air pressure above 12 lb. at the converter, keeping the slag above 17% in SiO_2 , and oiling the ends of punch-bars, which prevented them from sticking. Temps. were measured with a radiation pyrometer, sighted through a hole in the smoke-hood. Near the end of the blow the temp. was close to the freezing point. When the charge grew too cold, scrap iron was added; coal

was found to be of little use for this purpose. The first stage of the blow was taken only to a white metal of 70-72% Cu, so that a slag blanket remained on the charge during the second stage. With small charges (10-20 tons of mat) there was little slopping of charge, and collars of cold material at the mouth of the converter were made easily removable by dressing the mouth with clay before each blow. Secondary material was charged from an overhead hopper so that it was not necessary to interrupt the blow. Preheating of the blast by waste gases from the converter is suggested for 65% mats, but was not tried. The same ladle was used for the pour of blister as for the slag, the coating of chilled slag forming an excellent lining. A. BUTTS

The manufacture of tin-plate and the electrolytic detinning process. GEORGES VIG. *L'âge de fer* 36, 763-5(1920).—Description of the modern method of tin-plate manuf., and of the various methods used and proposed for detinning waste tin-plate. A. P.-C.

Tinning methods and tin-house equipment. C. F. POPPLETON. *Iron Age* 107, 187-92(1921).—An illustrated description of the tinning process, the tin-house equipment and layout. A novel departure, from the usual hand-fed tinning pots, consisting of an automatic machine which feeds, pickles and polishes four plates at once, with the plates traveling straight forward throughout the process, is described. Inability to inspect the plates between the white pickling and before tinning is an outstanding fault. W. H. BOYNTON

Melting brass with fuel oil. S. D. RICKARD. *Metal Ind.* 18, 460-3, 507-10(1920).—R. claims that fuel oil, when properly used, is to-day the most satisfactory and economical fuel for the melting of brass and other non-ferrous metals. The low pressure system is advocated. Each phase of "The Oil Burning System" is taken up in detail with sufficient sketches for reproduction. A. W. OWENS

A novel core oven. STEPHEN B. PHELPS. Pittsburgh. *Metal Ind.* 18, 503(1920).—Instead of using the usual track to support the core trucks, "I" beams and trolleys were used to support them from overhead. This arrangement removed the supporting elements from the zone of most intense heat. The ends of the trucks were made as oven doors so that when one truck was drawn out for reloading, the back end of the truck acted as a door and closed the oven, permitting access to one truck while the cores on the other truck were baking. A. W. OWENS

Steel sand properties. R. L. LINDSTROM. *Foundry* 48, 940-3(1920).—Lab. tests should precede large purchases of sand or clay for steel foundry purposes. Both sand and clay should be of the same high quality. The ideal clay will have both high bonding power and a high softening point. For the bonding tests 10% clay is mixed with 90% of a good sand and with enough water so that the mixt. will just adhere to the palm of the hand. Knead for exactly 2 min. and age in a covered receptacle for 12 hrs. A block 1 by 1 by 12 in. is made under uniform pressure and is pushed lengthwise over the edge of a glass plate until it breaks off. Considering 3 in. as 100, the length breaking off is the bonding strength. The following specifications will designate a good clay: bonding strength 85, softening point 1600°, fineness test, not more than 5% shall remain on a 20-mesh sieve and not less than 75% on a 100-mesh. A good sand will be high in silica (97-99%); 85% should be retained on the 20, 40, and 60 mesh screens and the grains should be well rounded. A. W. OWENS

The determination of the temperature of liquid steel under industrial conditions. ANON. *Russ. Min.* 51, 27-9(1919).—In controlling the manuf. of steel in a Martin furnace it is important to be able to measure accurately the temp. of the molten steel. An optical pyrometer is the only suitable device for this purpose. Since it is claimed that an observer with a blue glass can with his eye alone estimate temps. to within 15°, it is suggested that to be worth while a pyrometer must be capable of measuring to within 10° better. The precautions to be observed in the practical measurement of temp.

are enumerated. It is recommended that the instrument be placed at a distance of 4 meters or less from the flowing steel. At greater distances the temps. may appear too low (by as much as 40°) due to the intervening smoke and fumes and to the fact that the field of the instrument may not be completely filled. Some actual measurements with a Fery radiation pyrometer are recorded and the true temps. are calcd. from the apparent temps. on the assumption that the emissivity of the slag is 0.50 and that of the steel is 0.40. In practice the furnace itself may be made to serve as a pyrometer. At low temps. the flame is easily visible, but as the temp. is raised it becomes less distinguishable and at about the temp. at which silica bricks begin to melt it is no longer possible to see the flame. At this point the flame is lowered until temp. differences are again noticeable.

L. H. ADAMS

Temperature measurements in steel furnaces. GEORGE K. BURGESS. Bureau of Standards. *Chem. News* 121, 280-91(1920).—Summarizes the situation (cf. C. A. 14, 377; 13, 2838, 2839). Correlation of temp. observations with technical experience is now the principal need.

W. P. WHITE

The metallurgical laboratories of the steel plant at Essen. GEORGES VIF. *L'âge de fer* 36, 664-6(1920).—A description of the laboratories of the Krupp plant at Essen.

A. P.-C.

The industrial uses of ferro-silicon. JHAN VISCARD. *Industrie chimique* 7, 380-91(1920).—A brief review of the use of ferro-Si in metallurgy (reducing the amt. of C in cast Fe), for special steels (for springs, automobile gears, rails), in the manuf. of generators, motors and transformers, for acid-resisting alloys (métallure, élanite, duriron, ironac, tantiron), for explosives (mixt. of an oxidizing agent, ferro-Si or Si, high boiling petroleum residue rich in naphthalene, and a nitro explosive), and for the prepn. of H (by the action of NaOH).

A. P.-C.

Ferro-alloys. ED. LIEVENIE. *L'âge de fer* 36, 733-5(1920).—A review of the method of prepn. and industrial uses of ferro-Mn, ferro-Si, ferro-Cr, ferro-W, ferro-Mo, ferro-V, ferro-B, ferro-U.

A. P.-C.

Electrolytic iron. A. VO. *Chem. Weekblad* 16, 417-9(1919).—A brief note on the history of electrolytic Fe and on the properties of the most recent product.

L. H. ADAMS

Waste disposal from war manufactures (STROOFF) 14. The corrosion of metals by the phenols of low-temperature tar (EHRHARDT, PFLEIDERER) 21. Pyrite in the Huelva District, Spain (DE KALB) 8. Static notched-bar testing machine (ANON.) 1.

Ore flotation. W. A. SCOTT. U. S. 1,385,281, Jan. 11. Bubbles of air carrying acid are formed in a free-flowing ore pulp containing a substance such as soap which is capable of reacting to produce a flotation agent and the bubbles and attached solids are sepd. from the remainder of the pulp.

Ore flotation apparatus. JAS. B. BROWN. Can. 208,077, Feb. 1, 1921. The app. comprises a container divided into a feed chamber, a sepg. chamber provided with an overflow and a transfer conduit. This conduit communicates with each of the chambers near the bottom, and has an outlet adapted to deliver material in sheet-like form on to the liquid level in the sepg. chamber. Means is provided for introducing a gas into the lower part of the transfer conduit.

Flotation machines. D. P. HYNES. Can. 208,135, Feb. 1, 1921. The app. comprises a tank divided into two chambers and laterally spaced for laminated rotary disks partially submerged in the pulp contained in one chamber and adapted when rotated to entrain air from above the surface of the pulp and carry it into the same chamber where it is liberated as bubbles to form a froth and cause the froth to be discharged into the other chamber at a point below the upper edges of the disks.

Apparatus for concentrating ore by flotation. G. GRÖNDAL. Can. 208,204, Feb. 1, 1921.

Concentration of ores. H. R. ROBBINS. Can. 208,256, Feb. 1, 1921. Ores containing sulfides of Cu and Fe are concd. by adding a non-alk. salt to freely flowing pulp of ore, without an org. frothing agent, producing fine air bubbles in the pulp, collecting and sepg. the froth formed.

Concentrating ore. R. LUCKENBACH. Can. 208,212, Feb. 1, 1921. Ore pulp is passed through one or more screens composed of excelsior coated with oil or grease which may or may not be mixed with liquid rubber. The mineral values adhere to the screen and the gang is rejected.

Frothing and mineral selective composition and process of making and using same. R. LUCKENBACH, Can. 208,213, Feb. 1, 1921. The reaction product of KMnO_4 and a resin with or without NH_3 is used as a frothing and mineral selective agent.

Mineral selective agent and method of using the same. R. LUCKENBACH. Can. 208,210, Feb. 1, 1921. Finely divided ore is mixed with water to form a pulp and the pulp is directed against a surface consisting of petroleum grease and rubber to which the mineral content will adhere and then sepg. the mineral from the material. A moving belt may be used as the surface to which the selective agent is applied.

Apparatus for reducing and smelting ores. J. LUND. U. S. 1,365,113, Jan. 11. The app. is adapted for reducing unbriqueted ore with either liquid or solid fuel.

Recovering metals from ore by treatment with mercury. S. G. MUSSER. U. S. 1,365,844, Jan. 18. A hollow rotating column of ore is passed by centrifugal force through a hollow body of Hg and tailings are discharged in a direction opposite to that of the rotation to prevent too close packing of the material in the column.

Recovering mercury. H. W. MATHESON. Can. 208,348, Feb. 8, 1921. Hg is recovered from sludge by sepg. the Hg from the other ingredients by washing, then heating to 100–500° to decompose Hg compds. and coalesce the free Hg particles, then dry grinding the remaining mass to sep. metallic Hg, again heating to 100–500° and wet treating to remove non-mercuric matter.

Separating zinc sulfide from lead sulfides in ores. L. BRADFORD. Ger. 321,159, Sep. 17, 1913. The ore or concentrate is first pulverized and slimed, in order to sep. the various sulfide particles from one another and from the gang. The comminuted material is then subjected to a froth flotation process and to stirring and air flotation processes, oleic acid being used, with heating, as the frothing agent. A soln. of NaCl, acidified with H_2SO_4 and rendered neutral or alk., is employed. The optimum temp. range is 49–71°.

Mechanically operated Scotch hearth. A. S. MOSES. Can. 208,372, Feb. 22, 1921. The pat. specifies a smelting furnace which has a stationary hearth, a poker, a movable support for said poker, means for moving the poker into the material on the hearth and means for moving the support. Cf. C. A. 14, 529.

Heat-treating furnace. CHAS. J. KIRK. Can. 208,731, Feb. 22, 1921.

Metallurgical smoke filter. WM. H. BATES, JR. Can. 208,639, Feb. 22, 1921.

Apparatus for drawing billets from a furnace. ALBERT SODERSTROM. Can. 208,901, Feb. 22, 1921. Structural features.

Heat treatment of wire or sheet metal. RANDAL E. TALLEY. Can. 208,856, Feb. 22, 1921. Wire or sheet metal is heated by passing it through a tunnel closely adjacent to a strip of highly heated metal, the latter being heated by elec. or other means. App. is also specified.

Metal surfacing by centrifugal force, using finely divided metals in conjunction with reducing agents. METALLISATOR, G. M. B. H. Ger. 318,460, Mar. 23, 1915. The reducing agent is converted into the colloidal state and brought into contact with the metal. E. g., com. oildag or aquadag is run in a fine stream into molten vaseline,

the mass is allowed to cool and placed in a form provided with slits through which the wire of the metal used passes, thereby coating the wire with a thin uniform layer of the reducing agent.

Firmly adhering metal coatings on metal base. METALLISATOR, G. M. B. H. Ger. 318,461, Apr. 10, 1915. A thin layer of a readily fusible metal or alloy is applied first to the metal surface to be coated, and then the metal finally to be applied is projected against the surface at such a temp. that the first coating is melted. Sn and Wood's metal are mentioned as suitable for the first coating.

Applying protective coatings containing zinc to metal surfaces. C. MARK. Ger. 319,734, Aug. 25, 1915. A molten bath containing Zn is covered with a flux also containing Zn, and the Zn content of the bath is maintained constant by periodic additions of Zn. Upon immersion, an initial coating of an Fe-Zn alloy is formed on Fe or steel surfaces, so that the outer coating in the bath below the surface (say a Pb-Zn alloy) is facilitated and the uniformity of its compn. and properties is insured. The Zn is added preferably in the molten state, and in a slight excess.

Metallic reflectors. S. O. COWPER-COLES. Brit. 152,860, Oct. 15, 1919. In making a parabolic or other reflector, a chemically silvered glass mold is electrolytically coated with Fe, and the two metals are removed together. The Ag is then cleaned off by a cyanide or other soln. not attacking Fe, and the Fe is sherardized and finally polished.

Composite tubes. CROSBY STREAM GAGE & VALVE CO. Brit. 152,947, Oct. 11, 1920. Composite metal tubes for pressure gages have an outer tube of resilient metal such as steel and an inner tube of non-resilient non-corrosive metal such as very pure Cu. A suitable construction is specified.

Producing vanadiferous pig iron and steel. ARTHUR F. G. CADENHEAD and WM. M. GOODWIN. Can. 208,623, Feb. 15, 1921. Vanadiferous iron ore is furnaced with a reducing agent and a suitable flux to produce pig Fe having a max. proportion of V.

Making manganese steel. WESLEY G. NICHOLS. Can. 208,831, Feb. 22, 1921. To a weighed quantity of blown metal having a temp. of 3000° F. is added a sufficient quantity of Mn steel alloy at a temp. of 2400° F. to produce a steel having a Mn content of 11-14% and of proper pouring temp. The metal is then poured into molds. Cf. C. A. 15, 362.

Recovering manganese steel. WESLEY G. NICHOLS. Can. 208,832, Feb. 22, 1921. The charge of metal is heated by an initial application of heat not over 700° F., the temp. is increased in stages to bring the mass gradually to the m. p. of steel and finally to the point of high fluidity just previous to tapping. Cf. C. A. 15, 362.

Protecting iron or steel from corrosion during heat-treatment. S. WHYTE. U. S. 1,366,305, Jan. 18. A mixt. formed of fireclay 63, Na silicate 25, Na₂CO₃ 6 and fused borax 6 parts is applied to Fe or steel or like metals to protect their surfaces during heat treatment.

Borax-dextrin mixture for coating iron or steel. T. YOSHIZAWA. U. S. 1,365,760, Jan. 18. A mixt. of borax 5-15 and dextrin 2-5 parts is used for coating metals or as an addition to inks, disinfecting solns., etc., to prevent corrosion.

Protecting vessels from corrosion by metallic solutions. M. A. ADAM. U. S. 1,365,141, Jan. 11. Vessels of Fe or similar material containing solns. of corrosive substances such as solns. for detinning tinned Fe are protected from corrosion by attaching an anode of C or Sn to the vessel and passing an elec. current through it so that a metallic protective deposit is maintained on the vessel compensating for or preventing destructive action of the soln.

Alloys; iron and steel manufacture. E. C. R. MARKS. Brit. 152,840, Sept. 11, 1919. An alloy, particularly for use in refining Fe and steel, or in the production of steel alloys, consists of Mg and Si with or without Fe or Mn or both, the Mg being present in excess of the equi-mol. proportion to the Si. The alloys may contain 50-90%

of Mg, 10-40% of Si, and up to 10% of Fe; or 50-70% of Mg, 10-20% of Si, 10-20% of Mn, and up to 10% of Fe. In making the alloys, the Si may be supplied as ferro-silicon, and the Mn as ferromanganese.

Steel alloy. H. S. FOOTE. U. S. 1,366,254, Jan. 18. An alloy steel adapted for making high-speed tools or gears is formed of steel alloyed with U 0.20-1%, Si 0.55-2%, Ni 2-3.5% and Mn 0.50-0.60%.

Aluminium alloy. A. DE LAVANDEYRA. U. S. 1,365,178, Jan. 11. An alloy susceptible of heat treatment and adapted for rolling, forging, extruding or swaging is formed of Al 96, Mn 0.5, Mg 0.5, Cu 2.5 and Cr 0.5%.

Alloying chromium with the surface of other metals. F. C. KELLEY. U. S. 1,365,499, Jan. 11. Metal articles such as Fe or steel are superficially alloyed with Cr by heating the metal under non-oxidizing conditions in contact with a powdered charge containing metallic Cr to a temp. between 1200° and the m. p. of the metal but below the latter.

Iron and chromium alloys. A. W. CLEMENT. U. S. 1,365,091, Jan. 11. An alloy of Fe and Cr substantially free from C and oxides is prepd. by first reducing a combined ore of Fe and Cr, decarburizing the reduced metals by treatment with oxide of one or both metals and then deoxidizing the product by treatment with CaC₂ formed in an elec. furnace and with an excess of lime.

Ferro-chromium. T. GOLDSCHMIDT AKT.-GES. Brit. 152,990, Sept. 29, 1920. C-free ferro-chromium is obtained by the thermo-aluminic reaction of a mixt. of chrome Fe ore, Al or other reducing metal, and oxides of Fe, preferably roll scale. Oxides of other metals, such as Co, Ni, W, Mo, and V, may be added to produce the corresponding alloys.

Zinc-aluminium alloys. HEDDERNHEIMER KUPFERWERK UND SÜDPREUSSISCHE KABELWERKE, AKT.-GES. Ger. 318,346, Jan. 18. 1917. In a process of toughening Zn-Al alloys with 10-60% Al, the alloys are subjected to a mechanical treatment at a temp. above the Zn rolling temp. (120-150°), and then after-treated by heating to a higher temp.

Alloy of great hardness for tools and utensils. GES. FÜR WOLFRAM-IND. M. B. H. Ger. 320,996, Apr. 3, 1918. Addition to 310,041: The alloy of 310,041 consists of W, Fe, Ti, C and some Ce, in which the content of W may be as high as 60%. A small amt. of Cr (ferrochrome) may be added when great hardness and a low degree of brittleness is desired. E. g., the alloy may be composed of W 60, Fe 26, Cr 4, Ti 5, C 3 and Ce 2.

Pyrophoric igniters and illuminating devices. KUNHEIM & Co. Brit. 153,306, Nov. 1, 1920. Shaped bodies of pyrophoric Ce alloys for ignition and illuminating purposes are obtained by pressing or drawing the alloy under high pressure through openings in sufficiently hard material, such as steel, diamond, stone, and the like, the alloy being preferably warmed. The product may be of angular, circular, or oval cross-section and may be hollow or solid.

Electric welding of metals. F. L. SESSIONS. U. S. 1,365,198-9, Jan. 11. Elec. and mechanical features.

10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

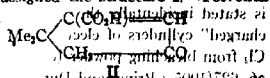
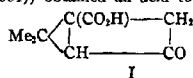
Aromatic hydrocarbons. A. MAILHE. *J. usines à gaz* 44, 353-5(1920).—A review of some of the more recent studies made on the production of homologs of benzene by natural and synthetic means.

J. L. WILBY

Observation on the note of Drs. Schneider and Schellenberg on the constitution of the humic acids. M. POPP. Oldenberg. *Brennstoff Chem.* 2, 11(1921); cf. Popp, C. A. 15, 372, and Schneider, and Schellenberg, C. A. 15, 429.—Polemical. W. B. V.

Chemistry of polycyclic structures in relation to their homocyclic saturated isomerides. I. Some derivatives of cyclopentene and dicyclopentene. HAROLD FARMER AND CHRISTOPHER KELK INGOLD. *J. Chem. Soc.* 1920, 1783-1798 (1920).

—In the degradation of the product obtained by condensing Et $\text{CH}(\text{CO}_2\text{H})_2$ with dimethylglutarate with $\text{CH}_3(\text{CO}_2\text{Et})_2$ by NaOEt, Perkin and Thorpe (*J. Chem. Soc.* 79, 729 (1901)) obtained an acid to which they assigned the structure I. To which



(C. A. 14, 1311) has since obtained this same acid from β, β' -dimethyl- α, α' -dicapric acid in the KMnO_4 oxidation of isodehydrodicapric acid (and has accordingly assigned to it the structure II. F. and I. have oxidized dimethylcyclopentene-2,3-dicarboxylic acid (A) (I with CO_2H replacing II in the CH_2 group) to trans-2,3-dibromo acid (B), $\text{Me}_3\text{C} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHCO}_2\text{H}$, thus proving the structure I for the product in

question. The theoretical part is most interesting and involves the assumption of some remarkable reactions, but cannot be readily abstracted. Oxidation of A in cold KMnO_4 soln. with 3% KMnO_4 gave $\text{H}_2\text{C}_2\text{O}_4$ and $\text{C}_6\text{H}_5(\text{CO}_2\text{H})\text{CH}_2(\text{CO}_2\text{H})\text{CO}_2\text{H}$. The same products were obtained with NaMnO_4 (2.5%) oxidized in K_2CO_3 soln. with $\text{K}_2\text{Fe}(\text{CN})_6$ added during 5 days, and left stand 5 days more, gave B, mp. 213°, which was thoroughly identified. No cis-acid, though the trans-B was also obtained by oxidation with H_2O_2 in alk. soln. (O. A. 14, 1311).

Acenaphthene series. I. Conversion of o-nitroamines into isoxazolidine oxides. FREDERICK MAURICE ROWE AND JOHN STANLEY HERBERT DAVIES. *J. Chem. Soc.* 1921, 1344-51 (1921).—An extension to the acenaphthene (A) series of the hypochlorite method of oxidizing o-nitroamines (cf. G. A. 16, 1358, 1419, 8, 1412; 11, 1900). 2-Nitro-3-aminoacenaphthene (B) was made by the method of Sachs and Mosbach (G. A. 6, 95), through 3-nitro-3-amino-3-propylamine, and 3-nitro-3-propylaminacenaphthene, the yields being resp. 89%, 71%, 92%, and 35% of the pure products. Excess of NaOCl soln. added to B in hot alk. aq. solution, gave 50% of acenaphthene-2,3-isoxazolidine (C), pale brown needles, mp. 177°, odorless, non-volatile with steam, on heating with Zn dust gives NH_3 and C_{12}H_8 . B with at least 4 mols. $\text{NH}_4\text{OH} \cdot \text{HCl}$ in alc. made alk. with NaOH at 50°, and heated 20 min. at 60°, acidified with AcOH , diluted with dil. NaOH , and reprecip. with AcOH , gave acenaphthene-2,3-quinone dioxime (D), brown amorphous powder, does not melt below 300° with NaOH . C was reprecip. by reprecip. in dil. NaOH and steam distilled; it yielded a small quantity of acenaphthene-2,3-isoxazolidine, yellow needles from AcOH , mp. 143-4°. Acenaphthene-7,8-quinone dioxime (E) (Francesconi and Ruzicchi, *Ann. chim. ital.* 33, 1, 88 (1903)), mp. 220° (decomps.), dissolved in dil. NaOH and boiled with excess NaOCl till the color ceased to change, gave acenaphthene-7,8-isoxazolidine oxide (F), pale pink needles from alc., mp. 190°. E is readily reduced by NH_4OH to D (stated in one place to be the 1,2-dioxime). Acenaphthenequinone (G) (10 g. in 50 cc. concd. H_2SO_4) was nitrated with 1 mol. HNO_3 (d. 1.82) in 2 vols. concd. H_2SO_4 and reprecip. by adding 30 vols. 82% of aq. 4-nitrophenylhydrazine (H) was obtained and purified by warming with Na_2CO_3 in dil. AcOH and reprecip. from AcOH ; it was a yellow needles, mp. 218°, gave a red color with NaHSO_4 and brown color with dil. alkali and with hot concd. NaOH in alcohol. It was acidified, water and NaHCO_3 removed, H_2SO_4 removed, oxidation of G with $\text{Na}_2\text{S}_2\text{O}_8$ in AcOH gave the anhydride of 4,1,8-C₁₀H₆N₂O₄(CO_2H)₂, mp. 229-30°, which on distill. with CaO gave α -C₁₀H₆N₂O₄. The phenylhydrazone of G formed a red color with NaHSO_4 and brown color with dil. alkali and with hot concd. NaOH in alcohol. Acenaphthenequinone (H) (10 g. in 50 cc. concd. H_2SO_4) was nitrated with 1 mol. HNO_3 (d. 1.82) in 2 vols. concd. H_2SO_4 and reprecip. by adding 30 vols. 82% of aq. 4-nitrophenylhydrazine (I) was obtained and purified by warming with Na_2CO_3 in dil. AcOH and reprecip. from AcOH ; it was a yellow needles, mp. 218°, gave a red color with NaHSO_4 and brown color with dil. alkali and with hot concd. NaOH in alcohol. It was acidified, water and NaHCO_3 removed, H_2SO_4 removed, oxidation of H with $\text{Na}_2\text{S}_2\text{O}_8$ in AcOH gave the anhydride of 4,1,8-C₁₀H₆N₂O₄(CO_2H)₂, mp. 229-30°, which on distill. with CaO gave α -C₁₀H₆N₂O₄. The phenylhydrazone of H formed a red color with NaHSO_4 and brown color with dil. alkali and with hot concd. NaOH in alcohol. Acenaphthenequinone (J) (10 g. in 50 cc. concd. H_2SO_4) was nitrated with 1 mol. HNO_3 (d. 1.82) in 2 vols. concd. H_2SO_4 and reprecip. by adding 30 vols. 82% of aq. 4-nitrophenylhydrazine (K) was obtained and purified by warming with Na_2CO_3 in dil. AcOH and reprecip. from AcOH ; it was a yellow needles, mp. 218°, gave a red color with NaHSO_4 and brown color with dil. alkali and with hot concd. NaOH in alcohol. It was acidified, water and NaHCO_3 removed, H_2SO_4 removed, oxidation of J with $\text{Na}_2\text{S}_2\text{O}_8$ in AcOH gave the anhydride of 4,1,8-C₁₀H₆N₂O₄(CO_2H)₂, mp. 229-30°, which on distill. with CaO gave α -C₁₀H₆N₂O₄. The phenylhydrazone of J formed a red color with NaHSO_4 and brown color with dil. alkali and with hot concd. NaOH in alcohol.

Univ. Manchester. *J. Chem. Soc.* 117, 1529-34(1920).—S. has studied the Hoesch reaction (C. A. 9, 2541), using resorcinol with substituted imido chlorides. He has shown that the reaction probably proceeds in two steps. The imido ester is first formed at a temp. of about 50°, and on heating to 150° rearranges into the ketimine: $C_6H_4(OH)_2 + RC(=O)N:NR \xrightarrow{HCl} C_6H_4(OH)(OC(=O)R):NR \xrightarrow{heat} C_6H_4(OH)_2C(=O)R:NR$. The *anilide* of 2,4-dihydroxybenzophenone, prepd. by heating 3 g. benzanilideimido chloride with 2 g. resorcinol at 50° until the evolution of HCl had ceased and then to 150° for 10 min., finally sepd. as red oil on treating the mass with water. After several attempts there was obtained a small amt. of cryst. material from AcOEt, m. 228-30°. On hydrolysis of the oily material with alc. HCl 2,4-(HO)₂C₆H₂Bz was produced. The imido chloride from 5 g. carbethoxy-*p*-oxybenzanilide (C. A. 14, 1985) heated with 2.5 g. resorcinol for some time and then hydrolyzed gave 2,4,4'-(HO)₃CH₂COC₆H₄OH. Cinnamanilide imido chloride does not react normally but seems to give a benzopyrone deriv.

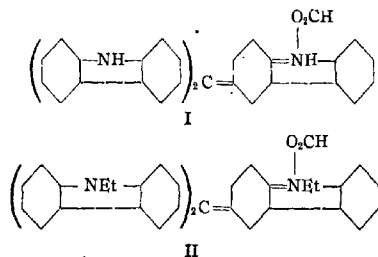
CARL S. MARVEL

Coumaranone series. I. The preparation of 4-, 5- and 6-methylcoumaran-2-ones, and some derivatives of *o*-, *m*- and *p*-tolylloxycetic acids. LUCY HIGGINBOTHAM AND HENRY STAPPHEN. Univ. Manchester. *J. Chem. Soc.* 117, 1534-42(1920).—New methods for the prepn. of a large number of compds. are described. Many of the physical consts. previously recorded by other observers were found to be incorrect. *o*-Tolylloxycetic acid (A), obtained in 150-g. yield by adding to 96 g. ClCH₂CO₂H at 110-120° during 2 hrs. 108 g. *o*-cresol and 100 g. NaOH in 400 cc. H₂O, then cooling and acidifying with 2 N H₂SO₄, crystals from alc.-m. 151-2°. NH₃ in dry Et₂O converts A to the *ammonium salt* (B), decomps. at 126°. The *acid chloride* (C), obtained in 20 g. yield by heating 20 g. A and 18 g. SOCl₂ to 60° for 15 min., removing the excess of SOCl₂ under 15 mm. and distg. *in vacuo*, b₁₀ 120°, m. 29-30°; *amide* (D), obtained in 90% yield from B by heating in an oil bath to 135° under 10 mm. until the H₂O was removed, crystals from alc. m. 127°. D is obtained also in the same yield from C and (NH₄)₂CO₃; *nitrile*, obtained in 6-g. yield by heating 10 g. D and 10 g. P₂O₅ to 120° for 15 min., then distg. under reduced pressure, yellow oil, b₁₀ 133°; *anilide*, from C and PhNH₂, crystals from alc. m. 108.5°; 4-methylcoumaran-2-one, obtained in 3-g. yield by slowly adding 8 g. AlCl₃ to 10 g. C in 15 g. PhH cooled in an ice bath and after 2 hrs. pouring into dil. HCl and distg. with steam, sepg. the PhH layer and distg. off the solvent, crystals from alc., m. 51°; *semicarbazone*, from alc., m. 228°; *oxime*, m. 143-4°; *p*-nitrophenylhydrazone, from dil. AcOH, m. 230-2° (decompn.). In exactly the same way and with the same yields *m*-cresol is converted into *m*-tolylloxycetic acid, m. 102°; *ammonium salt*, decomps. 188°; *chloride*, b₁₀ 126°, m. 19°; *amide*, m. 118°; *nitrile*, b₁₀ 141°; *anilide*, m. 95°; 5-methylcoumaran-2-one, m. 85°; *semicarbazone*, m. 208°; *oxime*, m. 156°; *p*-nitrophenylhydrazone, m. 214-6° (decompn.). *p*-Cresol gives *p*-tolylloxycetic acid, m. 135°; *ammonium salt* decomps. 177°; *chloride*, b₁₀ 124°, m. 17.9°; *amide*, m. 119°; *nitrile*, b₁₀ 136°, m. 38-39°; *anilide*, m. 109°; 6-methylcoumaran-2-one, m. 88°; *semicarbazone*, m. 227°; *oxime*, m. 148°; *p*-nitrophenylhydrazone, m. 195° (decompn.). The coumaranones give a purple color with FeCl₃, reduce Fehling soln., give a ppt. of Ag with Tollen's reagent and a deep red color with concd. H₂SO₄; their odor resembles hyacinth.

CARL S. MARVEL

Carbazole-blue and carbazole-violet. MAURICE COPISAROW. *J. Chem. Soc.* 117, 1542-50(1920).—A study of the carbinol and salts of carbazole-blue (I) and of "carbazole-violet" (II), dyes of the Ph₃CH type. I was prepd. by Suida's method (cf. *Ber.* 12, 1403(1879); also, Bamberger and Muller, *Ber.* 20, 1903(1887)). There was no improvement on the 5% yield by using anhydrous (CO₂H)₂, ZnCl₂, AlCl₃, or by varying the temp.; no I was obtained from carbazole (C₁₂H₉N), CCl₄, and AlCl₃. The prepn. of I and II indicates HCO₂H as a definite decomn. product of (CO₂H)₂ (cf. C. A.

13,128). KOH fusion of I yields $C_{12}H_8N$. *Tri-3-carbazylcarbinol*, $(C_{12}H_8N)_3COH$ (A), prep. by the method of Baeyer and Villiger (*Ber.* 37, 2873(1904)), prisms from PhMe, m. 117–8°; acetate, blue-violet; oxalate, green-blue; sulfate, blue; nitrate, red-blue to purple. *Chloride of tri-3-carbazylcarbinol* $(C_{12}H_8N)_3C:C_{12}H_8NCl$, prep. by addition of HCl in C_6H_6 to I and a little BzOH in C_6H_6N , also by heating a suspension of $C_{12}H_8N$ in excess O_2NCCl_3 , a sluggish and incomplete reaction leaving 90% $C_{12}H_8N$ unchanged, fine blue granules from alc., decomp. above 300° without melting, practically insol. in H_2O or C_6H_6 , fairly sol. in alc., glacial AcOH, or C_6H_6N . Formate (I), prep. from A, is identical with the product of S. and of B. and M. *Tri-3-carbazylmethane*, $(C_{12}H_8N)_3CH$ (B), prep. from I by the method of B. and M., and obtained in very small amt. in the prepn. of I and from the reaction of $C_{12}H_8N$ and O_2NCCl_3 , rhombic needles from Et_2O , m. 217–8°; oxidation with acid $KMnO_4$ or with $O:C_6Cl_4:O$ and AcOH yields the corresponding colored salts of A. II, prep. from 9-ethylcarbazole like I, fine violet powder with metallic luster with general properties like I, practically insol. in H_2O or C_6H_6 , fairly sol. in alc. or glacial AcOH, chars without melting; the product obtained by the ready sulfonation in the cold gives a blue-violet aq. soln. *Chloride of tri-9-ethyltri-3-carbazylcarbinol* $(C_{14}H_{12}N)_3C:C_{14}H_{12}NCl$ (C), obtained by gradually adding 40 g. $AlCl_3$ to a mixt. of 55 g. (2 mols.) $C_{14}H_{12}NEt$ and 24 g. (1 mol.) CCl_4 in 400 cc. CS_2 , heating 8 hrs. on the H_2O bath and working up the mixt. in the usual manner (yield, after C_6H_6 extn., 87%), is a violet powder with Cu luster and the general properties of I and II. *Tri-9-ethyltri-3-carbazylmethane*, $(C_{14}H_{12}N)_3CH$, prep. by reduction of II and of C, and by condensation of $C_{14}H_{12}NEt$ with $CHCl_3$ and $AlCl_3$, where a compd. of Ph_3CH_2 type was indicated but not isolated, short needles from Et_2O and C_6H_6 , m. 186–7°; heated with HI and Al-Hg it yields B. *Tri-9-ethyltri-3-carbazylcarbinol*, $(C_{14}H_{12}N)_3COH$ (D), prep. like A, needles from Et_2O , then C_6H_6 , m. 92–3°. The formate prep. from D is identical with II.

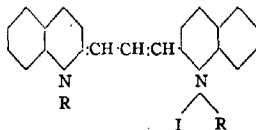


H. GILMAN

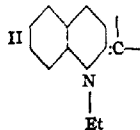
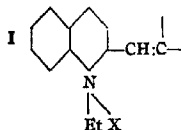
Dihydronaphthalene series. I. The *ar*-dihydro- α -naphthylamines and their derivatives. FREDERICK MAURICE ROWE AND ESTHER LEVIN. Municipal Coll. Techn., Manchester. *J. Chem. Soc.* 117, 1574–9(1920); cf. *C. A.* 14, 2927.—A continuation of work on dihydro- α -naphthylamines and derivs. with a view to their application in dye technology. *5,8-Dihydro- α -naphthylamine* (A) is prep. by slow addition of 34 g. α - $C_{10}H_7NH_2$ in a slight excess of dry EtOH to a boiling mixt. of 400 cc. naphtha (b. 139°) and 30 g. Na; when the Na is used up, the mixt. is poured into H_2O , the naphtha layer sep. and acidified with HCl, and the naphtha removed by steam distn.; the hydrochloride crystd. from the filtrate of the residue gives with alkali the free base; the pressed crystd. base was melted with 10% PhMe by wt., cooled, quickly filtered, and dried, 21 g. crude base and 15 g. BzH give *benzylidene-5,8-dihydro- α -naphthylamine* (B), massive rhombic pyramids from petroleum, m. 69° (cor.). HCl hydrolysis of B yields pure A, rhombic plates or needles, m. 37.5° (cor.), b₁₀₀ 247°. *Hydrochloride*

(C), stout needles. 1,4-Dihydronaphthalene is obtained by diazotization of A and reduction with Na_2SnO_2 . 5,8-Dihydroaceto- α -naphthalide, silky needles from alc., m. 163° (cor.). 2,4-Dinitrophenyl-5,8-dihydro- α -naphthylamine (D), obtained by refluxing 5 g. A, 6.9 g. $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{Cl}$ in 100 cc. alc. and 4.8 g. crystd. NaOAc in a little H_2O , red-brown plates from AcOH or PhMe, m. 144° (cor.). Sodium *p*-sulfobenzeneazo-5,8-dihydro- α -naphthylamine (E), obtained by adding diazotized $p\text{-H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}$ to aq. C, cryst. ppt. which, dissolved in the minimum boiling dil. aq. Na_2CO_3 , gives glistening brown plates. 7,8(or 5,6)-Dihydro- α -naphthylamine (F), prepd. like A except that the mixt. was distd. when the Na disappeared until the internal temp. reached 140°, when heating was maintained for 1 hr. (some NH_3 was evolved with decompn. of the base), colorless oil, b_{34} 180–2° (does not cryst. at –18°), quickly darkens on air exposure and is less stable than A. Hydrochloride, straw-colored feathery needles, more sol. than C. 1,2-Dihydronaphthalene, obtained by diazotization of F and reduction with Na_2SnO_2 . Benzylidene-7,8-dihydro- α -naphthylamine, prism-pyramids from light petroleum, m. 64° (cor.). 7,8-Dihydroaceto- α -naphthalide (in poor yield), silky needles, m. 153° (cor.). 2,4-Dinitrophenyl-7,8-dihydro- α -naphthylamine, prepd. like D, red-brown leaflets or needles, m. 136° (cor.). Sodium *p*-sulfobenzeneazo-7,8-dihydro- α -naphthylamine, prepd. like E, red-brown glistening plates. *ar*-Tetrahydro- α -naphthylamine (G), obtained by adding 15 g. Na to 100 g. F in 200 cc. boiling dry EtOH. Benzylidene-*ar*-tetrahydro- α -naphthylamine, prepd. from G, flat rhombic prisms from light petroleum, m. 61.5° (cor.). A table of color comparisons is given for azo dyes from $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$, A, F, and G with $\beta\text{-C}_{10}\text{H}_7\text{OH}$ and $p\text{-H}_2\text{NCH}_2\text{H}_2\text{SO}_3\text{H}$. H. GILMAN

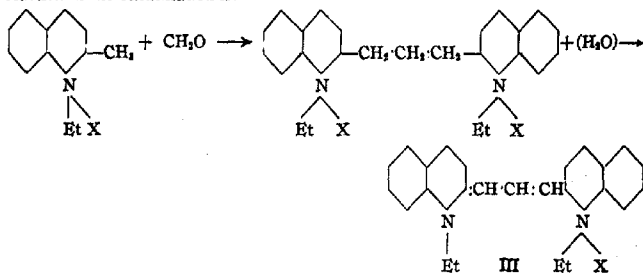
The cyanine dyes. III. The constitution of pinacyanol. WM. HOBSON MILLS AND FRANCES MARY HAMER. Cambridge. *J. Chem. Soc.* 117, 1550–62 (1920); cf. *C. A.* 13, 1393, 1448; 14, 3640.—The two different formulas previously suggested for pinacyanol (A) do not represent the compn. correctly since one of them contains one C atom less than analytical results indicate and the other, having two Me groups, does not agree with the behavior on oxidation. The formula which is most probable is:



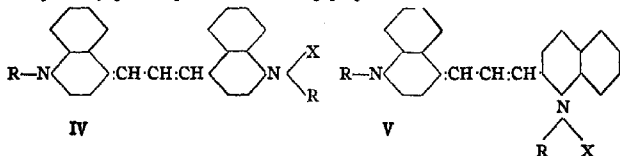
This formula is based upon the following facts. Halogen detns. show a mol. wt. of 479 ± 1 for 1,1'-diethylcarbocyanine iodide, showing that contrary to the views of O. Fischer it still contains the residue of 1 mol. CH_2O . The reaction for the formation of A is probably: $2\text{C}_{10}\text{H}_9\text{N.C}_2\text{H}_5\text{I} + \text{CH}_2\text{O} = \text{C}_{20}\text{H}_{18}\text{N}_2\text{I} + \text{H}_2\text{O} + \text{HI} + 2\text{H}$. The alkyl iodides of $\text{C}_{10}\text{H}_7\text{N}$ bases can take part in the carbocyanine condensation only if they contain a 2-Me group and in this condensation 2 mols. of alkyl iodide and 1 mol. CH_2O are concerned. Oxidation of the Br salt of A in dil. HNO_3 yields a cryst. quaternary nitrate which was shown to be quinaldinic acid ethyl nitrate (B) because of its properties and since it yields 1-ethyl-2-quinolone (C) on oxidation with $\text{K}_2\text{Fe}(\text{CN})_6$. These facts indicate that A contains the grouping I. While oxidation with dil. HNO_3 ,



splits off from the pinacyanol mol. the quinaldine residue containing the 5-valent N atom, KMnO_4 splits off the quinaldine residue containing the 3-valent N atom as ethyl-quinolone. This indicates a quinaldine residue is present in the form II. The main reaction in the condensation is:



In addition to dyes of the type III, IV and V should be possible of prepn. and would probably possess sensitizing properties similar to those of the other



members of this group. 1,1'-Diethylcarbocyanine bromide (D) was boiled under a reflux with dil. HNO_3 until the soln. became colorless, evapd. and dried over H_2SO_4 *in vacuo*, extd. with CHCl_3 , filtered and the CHCl_3 extd. with H_2O ; the aq. ext. was again evapd. and dried *in vacuo*; this residue washed with Me_2CO is B, m. 109° . B in H_2O slowly added to a soln. of $\text{K}_3\text{Fe}(\text{CN})_6$ and NaOH at $0-5^\circ$, extd. with Et_2O and evapd., yields C, m. $53-5^\circ$. Other products from the oxidation with HNO_3 were not identified. 1,1'-Diethylcarbocyanine acetate, prepd. by adding AgOAc to D, in boiling alc., filtering and evapg. the filtrate, was oxidized in Me_2CO at $0-5^\circ$ by slowly adding KMnO_4 until the color was permanent, filtering, freeing from Me_2CO under reduced pressure, extg. with Et_2O , washing with dil. HCl , filtered and drying over KOH , leaving a cryst. residue of C which was purified by vacuum distn. HCl was added to the aq. portions of the ext., evapd. and extd. with abs. EtOH ; the brown residue on evapn. of the EtOH was boiled with HNO_3 yielding B. Red salts (E) were obtained on warming D with dil. HNO_3 , pptg. the Br with AgNO_3 and warming the filtrate to $60-5^\circ$; this reaction is dependent on the production of oxides of N, as concd. acid not previously boiled and dild. causes the color change to take place below 60° ; if $(\text{NH}_2)_2\text{CO}$ is added no E is formed on boiling the soln. of D. E, which is a quaternary nitrate, was converted to the bromide (F) with KBr in hot H_2O ; after repeating the KBr treatment several times, F was recrystd. from H_2O and dried *in vacuo* at 50° ; it m. $201-2^\circ$ (decompn.); analysis gives $\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_4\text{Br} \cdot 2\text{H}_2\text{O}$. F on oxidation with dil. HNO_3 yields B and C.

N. A. LANGE

History of the preparation and properties of pure phthalic anhydride. C. E. ANDREWS. *J. Ind. Eng. Chem.* 13, 167-8(1921); cf. *C. A.* 14, 406, 3426; 15, 528.—The validity of the claim of A. (as given in his U. S. patent 1,336,182) to the manuf. of "phthalic anhydride in the form of colorless needle-like crystals substantially chemically pure and having a m. p. above 130° (corrected)" is discussed. G. W. STRATTON

Phenolic hexamethylenetetramine compounds. MORTIMER HARVEY AND L. H. BARKERLAND. Columbia Univ., N. Y. *J. Ind. Eng. Chem.* 13, 135-41 (1921).—In the bakelite reaction whenever NH_3 and HCHO are used, $(\text{CH}_2)_6\text{N}_4$ (A) is formed so that all results obtained by the use of NH_3 and HCHO can be duplicated with A alone. In the presence of PhOH A forms hexamethylenetetramine-triphenol (B), which by further action of heat gives off NH_3 and resinifies. A mixt. of 315 g. *m*-cresol and 136 g. A heated for 1 hr. in 50 cc. of 60% EtOH gave hexamethylenetetramine-*di-m*-cresol (D), long fine needles from 95% EtOH, m. 90° (decompn.). In H_2O a partial splitting of the mol. takes place, A dissolving and *m*-cresol forming as an oil. Splitting also occurs in Et_2O and Me_2CO , the *m*-cresol formed dissolving. A mixt. of 385 g. *p*-cresol and 167 g. A in 150 cc. of 95% EtOH heated on a steam bath for 1.5 hrs. gave hexamethylenetetramine-*di-p*-cresol (C), crystals from 50% EtOH which resinify at the m. p., 87° , and which decomp. and partially resinify when heated in a sealed tube for 3 hrs. at 90 – 100° . It has the same qual. soly. as D. A mixt. of 475 g. *o*-cresol and 205 g. A heated on the H_2O bath for 2.5 hrs. gave hexamethylenetetramine-*mono-o*-cresol, crystals from 95% EtOH which sublime and char on heating. Hexamethylenetetramine-quinol and hexamethylenetetramine-resorcinol (E) (*Ann.* 272, 282 (1892-3)) have no definite m. p. A (1 mole) and 3 moles carvacrol in 95% EtOH heated on the H_2O bath for 40 hrs. gave hexamethylenetetramine-carvacrol, crystals from 95% EtOH which resinify at the m. p., 148° , insol. in cold EtOH, sol. in Et_2O and Me_2CO . The following energy relationships were established: heat of soln. of A, 4.899 kg. Cal.; heat of soln. of PhOH , -2.89 kg. Cal.; heat of reaction of PhOH and A, 3.739 Cal.; heat of formation of A, -43.18 Cal.; heat of formation of PhOH , 50.96 Cal.; heat of soln. of B, -10.671 kg. Cal.; heat of formation of B, 19.06 Cal.; heat of combustion at const. vol. and at 20° of C, 8.008; of D, 8.010; of E, 6.715 Cal. per g. No general relationship between the chem. nature of these addition compds. and the substances from which they are formed is apparent. The results seem to indicate that the usual way of representing the structure of A is incorrect.

G. W. STRATTON

Catalytic hydrogenation of suberone. MARCEL GODCHOT. *Compt. rend.* 171, 1387-9 (1920).—Taboury and G. have shown (*C. A.* 6, 1750) that cyclopentanone (A) when reduced catalytically by H_2 and Ni gave cyclopentanol and α -cyclopentylcyclopentanone. Suberone (B) was obtained from suberic acid, which was prepd. by oxidizing castor oil (*Ber.* 26, 3069 (1893)) with HNO_3 . Sabatier and Mailhe (*C. A.* 3, 2675) obtained A from adipic acid, using MnO_2 , but B decompd. under the same conditions. When, however, the Ca salt (using 200 g. acid) was heated in tubes placed horizontally in an electrically heated furnace 45 g. pure B (yield 30%) were obtained under 10 mm. at 375 – 400° . NaHSO_4 was used to purify the product. B at 175° was converted into suberol (C), a liquid b. 184° , when subjected to the action of Ni and H_2 . When cycloheptane was subjected to the action of Ni and H_2 at 235° it was transformed into its isomer, methylcyclohexane (*J. prakt. Chem.* 49-50, 413). B at 240° gave a product b. 178 – 82° , a mixt. of B and C. The semicarbazone m. 163° and the phenylurethan m. 85° . No 6-membered ring was formed.

H. E. WILLIAMS

Modification of Skraup's quinoline synthesis. EDWARD DE BARRY BARNETT. *Chem. News* 121, 205-6 (1920).—The yield of quinoline (A) obtained when PhNH_2 (B) is heated with PhNO_2 , $\text{C}_2\text{H}_5(\text{OH})_2$ and concd. H_2SO_4 (Skraup, *Monatsh.* 1, 317; 2, 141; Walter, *J. prakt. Chem.* [2] 49, 549) is about 50% calcd. on the PhNH_2 used and only 27% of that theoretically possible with regard to the $\text{C}_2\text{H}_5(\text{OH})_2$. The use of H_2AsO_4 as an oxidizing agent in place of PhNO_2 (Kneuppel, *Ber.* 29, 709 (1896)) gives larger yields with reference to PhNH_2 but the process is wasteful of $\text{C}_2\text{H}_5(\text{OH})_2$, in that only 20% of the $\text{C}_2\text{H}_5(\text{OH})_2$ used enters into the reaction. Druce (*Chem. News* 117, 346 (1917)) prepd. A from the interaction of B as the chlorostannate with $\text{C}_2\text{H}_5(\text{OH})_2$ and H_2SO_4 . From 50 g. of the chlorostannate he obtained 20 g. A, which

is a yield of 80% with respect to B. In the equation $\text{PhNH}_2 + \text{Sn}(\text{SO}_4)_2 + \text{C}_6\text{H}_5\text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{N} + 3\text{H}_2\text{O} + \text{SnSO}_4 + \text{H}_2\text{SO}_4$, one mole of B requires the oxidizing power of a whole atom of Sn^{IV} and Druce's result is difficult to understand, since calcd. on the Sn^{IV} present his yield is 161% of that theoretically possible. Expts. were carried out in which B was treated with H_2SO_4 , $\text{Sn}(\text{SO}_4)_2$, and $\text{C}_6\text{H}_5(\text{OH})_3$. The yields of A were 30% of the theory provided the calcd. amt. of $\text{C}_6\text{H}_5(\text{OH})_3$ was used. If an excess of this reagent was used, the yields were poor. Better results were obtained when the cheaper reagent, $\text{Fe}_2(\text{SO}_4)_3$, was used and then only 60% yields were obtained. It seemed probable that the poor yields were due to the decompn. of the $\text{C}_6\text{H}_5(\text{OH})_3$ before the A formation had time to take place. The following expts. were carried out. (1) A great excess of $\text{C}_6\text{H}_5(\text{OH})_3$ was employed. (2) $\text{C}_6\text{H}_5(\text{OH})_3$ was added slowly to a heated mixt. of B, $\text{Fe}_2(\text{SO}_4)_3$, and H_2SO_4 . (3) The interaction took place at 130° . (4) H_2SO_4 , dild. to 80% strength was used. None of these changes so operated that the yields were improved. H_2BO_3 was added in the hope that a boric ester would be formed which would be more stable toward H_2SO_4 . This innovation has been of service in the prepn. of hydroxyanthraquinones (Bayer and Co. patents) but in the case of A formation H_2BO_3 had no effect at all. Poor yields are probably due not so much to the decompn. of $\text{C}_6\text{H}_5(\text{OH})_3$ as to the decompn. of B. It was found that B is easily destroyed at 140° when heated with H_2SO_4 and $\text{Fe}_2(\text{SO}_4)_3$. The best results are obtained with $\text{Sn}(\text{SO}_4)_2$ when 50 g. B are added to 75 cc. concd. H_2SO_4 and after the mixt. is cooled 50 g. $\text{C}_6\text{H}_5(\text{OH})_3$ and 190 g. $\text{Sn}(\text{SO}_4)_2$ are added. The mixt. is heated at $180-90^\circ$ in an oil bath for 6 hrs. The melt is then poured into H_2O . The free B is destroyed by the use of NaNO_2 and the soln. is made alk. and then A is steam-distd. The yields are 30% of the theory. When 150 g. $\text{C}_6\text{H}_5(\text{OH})_3$ were used there was only a small amt. of A formed. Better results were obtained when $\text{Fe}_2(\text{SO}_4)_3$ was used and this is the best method by which to make A in the lab. since the very violent reaction which often takes place when PhNO_2 and H_3AsO_4 are used is completely absent and there is no formation of tar. Dry $\text{Fe}_2(\text{SO}_4)_3$ need not be used, as calcined Fe_2O_3 treated with H_2SO_4 is equally as good. 40-50% yields of A may be obtained as follows. 100 g. B in 150 cc. concd. H_2SO_4 are added to 450 g. dry $\text{Fe}_2(\text{SO}_4)_3$ to which 370 cc. concd. H_2SO_4 has already been added 1 or 2 hrs. previously. 100 g. $\text{C}_6\text{H}_5(\text{OH})_3$ are added and the mixt. is heated 6 hrs. at $180-90^\circ$ in an oil bath. Without cooling, the mass is poured into H_2O containing NaOH and A and B are steam-distd. The distillate is acidified with HCl and NaNO_2 is added to get rid of B. The mixt. is heated for a few mins. until the PhN_2Cl has been destroyed and the soln. is made alk. and then steam-distd. A is extd. from the distillate with C_6H_6 and the ext. is dried over solid powdered NaOH and the C_6H_6 is then distd. off. Better yields (80%) may be obtained when the reaction is carried out as follows: 50 g. PhNH_2 and 65 g. $\text{C}_6\text{H}_5(\text{OH})_3$ with 100 g. calcined Fe_2O_3 are added as quickly as possible to 150 cc. concd. H_2SO_4 in an evapg. dish. A brisk reaction takes place at once and the mixt. should be stirred while it lasts. Afterward the mixt. is allowed to stand for 30 mins. without heating, and it is then poured into H_2O and the material is handled as in the other cases. Several hundred g. A have been prepd. by this method. FeSO_4 and SnSO_4 are readily oxidized by atm. O_2 , so that it seemed possible to obtain a catalytic process for making A. However, the reaction is slow, probably owing to the insoly. of the catalyst. In the process $\text{C}_6\text{H}_5(\text{OH})_3$ must not be decompd. by the H_2SO_4 and this condition is obtained by dilg. the acid to 80% and then working at $130-40^\circ$. A trace of $\text{Fe}_2(\text{SO}_4)_3$ or $\text{Sn}(\text{SO}_4)_2$ may be used as a contact substance but the latter is better. The reaction is slow for a lab. method, but indications are that with O_2 under pressure better results are possible, and the process appears feasible should a demand for A arise. H. E. WILLIAMS

New indicator. R. W. KINKRAD. *Chem. News* 122, 4-5(1921).—Moreau (*Compt. rend.* 132, 838(1901)) studied the effect of MeNO_2 on MeMgI , obtaining dimethyl-

hydroxylamine and Sand and Singer (*Ann.* 329, 190(1903)) stated that nitrosoallyl-hydroxylamine resulted from the action of NO on C_6H_5MgBr . No work appears to have been done on the effect of aromatic Grignard reagents on the *o*-NO₂ group. When EtNO₂ interacts with PhMgBr a deep blue soln. results which has properties of an indicator, turning pink with acids and blue with alkalis. One equiv. of EtONO₂ is added gradually to 1 equiv. of PhMgBr cooled in ice. A vigorous reaction takes place in a few mins. with evolution of heat. The mixt. is allowed to stand overnight. Then ice is added and, after the mixt. has stood for a few hrs. to allow Mg compds. to settle, the ether layer is removed and the ether is distd. off. Solid Na₂CO₃ and H₂O are added and the mixt. turns blue. The blue soln., obviously that of a Na salt, of the indicator cannot be kept long except as a very dil. soln. The ether soln. of the free indicator keeps well and the Na salt soln. was acidified and the free red indicator was extd. with Et₂O. As is the case with phenolphthalein, the indicator cannot be used in the presence of CO₂. Data are given showing that the indicator is very sensitive, the end-point is sharp as there is a radical change in color. Unfortunately the compd. is not very stable, and its indicating power is lost on standing. When the Et₂O soln. of the free indicator was evapd. the dark red liquor soon decompd. The free indicator and the Na salt are easily reduced by SO₂ but H₂O₂ has no effect. The depth of color shown by this compd. indicates that it has a high mol. wt. Evidently the Grignard reaction product has undergone further change. Further work on this compd. is in progress.

H. E. WILLIAMS

Electrolytic reduction of menthone. MOTOOKI MATSUI AND SHIU SHIMIZU. *Mem. Coll. Sci. Kyoto Imp. Univ.* 4, 245-64(1920).—The electrolytic reduction of hydroaromatic compds. containing the ketonic group has been studied by Tagel and Schmitz (*Z. Electrochem.* 8, 288(1902)), who reduced camphor in H₂SO₄ soln. to borneol. Brecht (*Ann.* 348, 200(1906); *C. A.* 3, 2797) obtained 2 isomeric borneolcarboxylic acids by reducing camphorcarboxylic acids in alk. soln. The ketone group, as in the case of ordinary ketones, is reduced to a sec. alc. group, but occasionally the CO group is changed to the hydrocarbon group (Piccinini, *Gazz. chim. ital.* 32, I, 260(1902)) as when methylgranatanine is produced from methylgranatonine. The reduction of menthone (A) was effected only in H₂SO₄ or HCl soln. Pb and Sn amalgams were the best cathodes but free Pb, Sn, Ni and Hg were used. Reduction took place most easily with a Hg cathode, but it is not suitable since the yield of A is lowered owing to the formation of an oil (B). The current efficiency is in no case more than 25%. There was no reduction when Ni was used. B was found in every expt., accumulating on the surface of the cathode soln. B b. 178-81°, has a terpene odor which does not resemble that of A nor menthol (C) and the properties of B accord well with those of menthane. The amt. of H₂ consumed during the electrolysis is greater than that required for the conversion of A to C. The most favorable condition for the production of C with the least formation of B are given. A was prepd. from *l*-menthol by oxidizing it by Beckman's method (*Ann.* 250, 325). The cathode liquid, a mixt. of 25 cc. 75% H₂SO₄, 50 cc. 94% alc. and 5 g. A was placed in a beaker. A porous cup was the anode compartment, and the anode liquid was 75% H₂SO₄. A Pt wire anode was used and Pb-Hg was the cathode. The mixt. was cooled by ice and salt and 4 amps. were used during 4 hrs. C is more sol. in alc. than A. The amt. of B increases when the acid strength is lowered. When 25% H₂SO₄ was used, about 3 g. B were obtained. The cathode liquor, after the run, was dild. with H₂O and extd. with Et₂O and the soln. was evapd. The residue was taken up in alc. and warmed with NH₂OH. Menthone oxime was removed but the residue of C did not cryst., due to the presence (unpublished work of D. Nishida) of impurities. Though A is absent, yet 33% of B are present. C was sep'd. from the reduction product in the form of its phthalic ester. A and B were found to dist. first with steam, and then the ester was hydrolyzed and the mixt. was steam-distd. C was

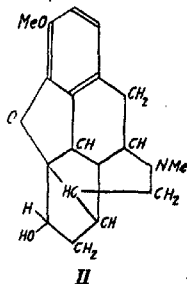
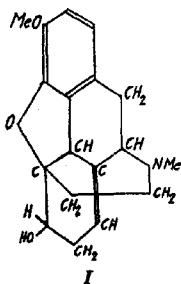
detd. quant. by heating the reduction product with Ac_2O and the acid which remained unchanged was titrated with standard NaOH . Tables are given showing conditions under which 14 expts. were run.

H. E. WILLIAMS

Constitution of the salts of aminoacetophenones. MITSURU KUHARA, HEIKICHI SAITO AND AKIRA SHIMOMURA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 4, 201-15(1920).—Close analogy in chem. behavior has been found to exist between the salts of the *o*- and the *p*-isomers of $\text{NH}_2\text{C}_6\text{H}_4\text{Ac}$ (A), but those of the *m*-series show a totally different character. When colorless *p*-A.HCl is heated for several hrs. at 100° it acquires a deep yellow color, which fades on standing. The colorless and colored salts in alc. exhibit the same color, which greatly weakens as HCl is passed into the soln. In H_2O the salts are almost colorless. *o*-A.HCl on heating turns and remains orange and the colored salt dissolves in H_2O and in alc. with an intense orange color, while the colorless salt in freshly prepd. aq. soln. or in alc. is almost colorless, but eventually alc. solns. of both salts assume the same color. The orange alc. soln. with HCl becomes weaker in color. The mono-Me deriv. (B) turns orange-red. *m*-A.HCl is colorless and undergoes no color change. Probably the colorless and yellowish salts of *p*-A are readily transformable to each other in alc., while the change in the case of the *o*-isomer is extremely slow. Conjecturally, the colored salts are quinoid and the colorless salts benzenoid and a reversible isomeric change of the keto-enol type may take place. $p\text{-ClH}_2\text{H}_2\text{NC}_6\text{H}_4\text{COMe} \rightleftharpoons \text{ClH.HN:C}_6\text{H}_4\text{:C(OH)Me}$. *m*-A and C cannot undergo isomeric change to the quinoid form but B may take the quinoid form, as it carries a moveable H. Conclusions are drawn from Baly and Marsden's work (*C. A.* 3, 1012) and the exptl. work of K., S. and S. coincided with their views. B. and M. state that the *p*-isomer shows the deepest absorption band, next the *o*-, and the *m*-isomer shows the lightest. The colored *o* and *p*-salts in alc. produce a new narrow absorption band toward the red at a greater concn. than the original band. The new bands of the 2 isomers are similar in depth and position and may be due to the quinoid form. The action of HCl seems to convert the quinoid into the benzenoid form. *m*-A and C and their salts do not manifest a second band, owing possibly to non-formation of the quinoid form. *p*-A was prepd. by a method suggested by Klingel (*Ber.* 18, 2688(1885)) from equimol. amts. of PhNHAc , Ac_2O and ZnCl_2 . *p*- $\text{Me}_2\text{NC}_6\text{H}_4\text{COMe}$ was prepd. according to the method of Rupe, Braun and Zembruski (*Ber.* 34, 3524(1901)). *o*-A and *m*-A were prepd. by the method of Camps (*Arch. Pharm.* 240, 6(1902)).

H. E. W.

Codeine. MARTIN FREUND, W. W. MELBER AND ERICH SCHLESINGER. Univ. Frankfurt. *J. prakt. Chem.* 101, 1-37(1920).—A critical study of the structure of codeine (A). The earlier works of Knorr, Pschorr and F. led to structure I for A. More recently Gadamer (*C. A.* 8, 2775), Braun (*C. A.* 8, 3303) and Freund and Speyer (*C. A.* 11, 1954) have shown that it probably does not contain aliphatic double linkages,



and that its structure should be represented by formula II. A series of reactions and derivs. of A have been now studied in order to obtain confirmatory evidence in support of formula II. Assuming that A has structure I, desoxycodine, prepd. by action of alc. and Zn on α - and β -chlorocodine, may be represented by 3 different formulas, depending on the position of the aliphatic double linkages. On reduction desoxycodine takes up 4 H, forming a tetrahydro base. The above 3 possible isomeric forms of desoxycodine would, however, all lead to the same tetrahydro base. On the other hand, if structure II is assigned to A the same reactions would give 2 isomeric tetrahydro derivs. The authors have now obtained by reduction of desoxycodine with Pd + H 2 isomeric bases, thus establishing exptl. evidence in favor of formula II. Dihydrocodine (B), prepd. according to the method of Oldenberg (D. R. P. 260,233) by reducing A with colloidal Pd + H, m. 86-9°, crystals from MeOH (O. gives 62-3°). It was unaffected by a boiling mixt. of CrO₃ and H₂SO₄, but when treated in glacial AcOH with concd. HNO₃ at low temp. yielded a *nitrodihydrocodine*, C₁₈H₂₆N₂O₄, yellow crystals from alc., m. 221°. Heated on a H₂O bath with MeI, B gave a *methiodide*, crystals from alc., m. 257°, which with dil. KOH yielded *des-N-methylidihydrocodine*, viscous oil; *methiodide* (1/2 H₂O), white leaves from alc., m. 173-6° (decompn.), gives with Ag₂O, KOH or Na-Hg vapors of NMe₃; *perchlorate*, crystals m. 201-2°. On reduction with Pd + H the des-base yielded *dihydro-des-N-methylidihydrocodine*, bright yellow sirup; *methiodide*, crystals from alc., m. 219-20°, or columns + H₂O, m. 221-4°, yields NMe₃ with alkalis. *Chlorodihydrocodine* was prepd. by slowly adding with cooling an emulsion of 10 g. PCl₅ and 20 cc. CHCl₃ to 10 g. B in 30 cc. dry CHCl₃, refluxing for 1-2 hrs., and pouring the mixt. into a large vol. of Et₂O. The sirupy product which sepd. was heated with Na₂CO₃, and the cryst. substance recrystd. from alc., tablets m. 172-4°. An additional amt. was obtained from the Et₂O. Yield 9.2 g. On boiling with H₂O, in AcOH it gave *chlorodihydrocodineamine oxide*, leaves + 3H₂O, m. 214° (decompn.). The latter was reconverted into the original Cl deriv. by action of H₂SO₄ in CHCl₃, and on nitration in AcOH yielded a *compound*, m. 223-4°, yellow cryst. powder. With MeI it gave a *methiodide*, fibrous needles from H₂O or alc. m. 244° (decompn.). The MeI deriv. readily gave *des-N-methylchlorodihydrocodine* when boiled in H₂O + few drops KOH, crystals m. 103°; *methiodide*, fine needles from alc. m. 272°, which are decompd. by alkalis, giving NMe₃. Reduction with Pd and H converted the des-base into *dihydro-des-N-methylchlorodihydrocodine*, bright oil; *methiodide*, fine needles from alc., decomp. 290-1°. Reduction of α -chlorocodine gave α -*dihydrodesoxycodine*, viscous oil which gave an oily *hydrochloride*, *methiodide*, *perchlorate*, and a solid *picrate*, *gold* and *platinum* salts. An isomeric *dihydro* base was obtained by electrolytic reduction of chlorodihydrocodine, large tablets from dil. alc., m. 117-9°. It was also prepd. by reduction of both β -chlorocodine and desoxycodine. It gave a *hydroiodide* when warmed in dil. AcOH with a few drops concd. aq. NaI, brown needles from H₂O, m. 245°. β -*Tetrahydrodesoxycodine* (C), obtained by reduction of desoxycodine-HCl (cf. Knorr and Hörlein, C. A. 1, 1285), seps. from MeOH or alc. with 1 mol. solvent, hexagonal leaves m. 147-8°, is weakly l-rotatory in alc. All attempts at further hydrogenation gave negative results, and despite its phenolic character, it yielded no Ac nor Bz deriv.; *hydroiodide*, long needles from H₂O m. 240-1°; *hydrochloride*, short prisms + 1EtOH, m. about 262°; *methiodide*, by digesting the base with MeI, crystals from H₂O, m. 263°. On evapn. with CNBr in CHCl₃, C remained unchanged. A quant. yield of *methoxytetrahydrodesoxycodine methiodide* was obtained by shaking a mixt. of 10 g. C, 25 cc. 10% NaOH and 15 cc. Me₂SO₄ until a clear soln. was obtained, and then adding concd. aq. KI, prisms from alc. + Et₂O, m. 255-6°. When heated with KOH it gave the *des-N-methyl base*, bright yellow oil; *hydroiodide*, crystals from alc., sinter 175°, and m. about 185°; *methiodide*, micropisms, sinter 185°, m. 188°, yields NMe₃ with boiling alkali, and a N-free yellow oil. The

addition of 0.8 g. Br in CHCl_3 to 1.43 g. C in 25 cc. CHCl_3 yielded *bromotetrahydro-desoxycodine*, needles from alc., soften 120° , m. 135° (decompn.). On reduction C is regenerated. The non-cryst. α -dihydrodesoxycodine gave on electrolytic reduction α -tetrahydrodesoxycodine, leaves from MeOH, m. $131-2^\circ$. Both the HCl and MeO derivs. m. at the temps. given by Knorr and Wäntig, 155° and 247° , resp.

D. BREHSE JONES

New derivatives of J-acid. W. KÖNIG AND H. HALLER. Dresden. *J. prakt. Chem.* 101, 38-57 (1920).—The I, Cl, and azo derivs. of J-acid (2,5-aminonaphthol-7-sulfonic acid) (A) could not be isolated directly on account of their great soly. and were, consequently obtained as their *p*-toluidine salts; 2-iodo-5-hydroxynaphthalene-7-sulfonic acid, prepd. by diazotizing A with NaNO_2 and H_2SO_4 , and boiling the product with HI, rose leaves from H_2O ; 2-chloro derivative, from the diazo deriv. and CuCl, gray leaves; 2-azo derivative, by diazotizing A and adding NaN_3 and AcONa , lustrous leaves; disodium salt, quickly darkens in the light. The following derivatives of A were further prepd.: 2-(β)-hydroxynaphthoquinoneimine, by adding to 16 g. of K 1,2-naphthoquinone-4-sulfonate in H_2O 12 g. of A in NaOH, and treating the violet-red product with HCl, amorphous, violet powder, sol. in H_2O and abs. alc., insol. in AcOH. The substantive, monoazo dyes obtained from this compd. give violet tones; 2-hydrasino (B), from diazotized A and $\text{SnCl}_2 + \text{HCl}$, aggregates of small white needles from H_2O , yield 70%, darkens in the light, especially when in alc., and reduces Fehling soln. β -Isatin-5-hydroxy-2-naphthylhydrazonesulfonic acid was obtained as the *p*-toluidine salt by boiling 5 g. B with 3 g. isatin for 6 hrs. and adding the calcd. amt. of $p\text{-H}_2\text{NC}_6\text{H}_4\text{Me.HCl}$, lemon powder, yield 82%. Its easily sol. Na salt has slight substantive dyeing properties toward cotton, while in dil. acids it gives to wool a greenish yellow tone. On boiling for several hrs. 6.2 g. of the $p\text{-H}_2\text{NC}_6\text{H}_4\text{Me}$ salt of the azo deriv. of A, 2.5 g. $\text{AcCH}_2\text{CO}_2\text{Et}$ and NaOEt (from 1.5 g. Na and 40 cc. alc.), hydrolyzing the brown reaction product with concd. NaOH and then acidifying with HCl, 1-[5'-hydroxy-2'-naphthyl]-4-carboxy-5-methyl-1,2,3-triazole-7-sulfonic acid was obtained as white needles. It gives bluish red azo dyes. Disodium dibenzoyl-5,5'-dihydroxy-2,2',1,1'-dinaphthylcarbazole-7,7'-disulfonate, prepd. by boiling for 8 hrs. 10.7 g. 2-hydrazino-5-hydroxynaphthalene-7-sulfonic acid with 120 g. NaHSO_4 (38°Bé.), neutralizing with NH_4OH , pptg. the sulfite with CaCl_2 , making the filtrate strongly alk. and finally stirring with 24 g. BzCl at $20-30^\circ$, crystals from H_2O or 95% alc. Its diazo salts give bluish red colors, stable to both alkalis and acids. Sodium dibenzoyl-2-amino-5-hydroxynaphthalenesulfonate, prepd. from A and BzCl , forms silky needles from dil. alc. With PCl_5 it readily yields the sulfonyl chloride, pale yellow glassy compd., m. 151° . With PhNH_2 the Cl deriv. gave the corresponding anilide, cryst. flakes when pptd. from alc. with dil. HCl, m. 155° . The di-Bz deriv. yielded on heating for 1 hr. with dil. NaOH 2-benzoylamino-5-naphthylsulfonanilide, yellow powder m. 125° . It gave with diazotized $p\text{-H}_2\text{NC}_6\text{H}_4\text{Me}$ a bright, yellow monoazo dye. When the above SO_2Cl deriv. in dry C_6H_6 was boiled with AlCl_3 an 81% yield of 2-benzoylamino-5-hydroxynaphthyl phenyl sulfone was obtained, yellow powder. Its Na salt forms a brown color with diazotized $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$.

D. BREHSE JONES

Influence of substituents on reactions. IV. The more favored substitution positions in 2-aminonaphthalene. HARTWIG FRANZEN AND GUSTAV STÄUBLE. Karlsruhe. *J. prakt. Chem.* 101, 58-74 (1920).—Only 3 Br atoms can be readily substituted in $2\text{-C}_{10}\text{H}_7\text{NH}_2$ (A). The first enters position 6 as shown, though not conclusively, by Claus and Philipson (*J. prakt. Chem.* 43, 47 (1891)). The third Br substitutes in position 3, and not in 4 as reported by Claus and Jack (cf. *Ibid* 57, 13 (1898)). Consequently the following changes in the formulas of the derivs. described by C. and J. should be made: 4,6-dibromo-1,2-naphthoquinone to 3,6-dibromo-1,2-naphthoquinone; the corresponding quinol to 3,6-dibromo-1,2-dihydroxynaphthalene, and the $\text{C}_{10}\text{H}_7\text{Br}$

obtained by deaminizing the corresponding NH_2 deriv. to 1,3,6-tribromonaphthalene. Bromination and reduction studies of A led to the following conclusions: Br substitutes in A the most readily in positions 1, 6 and 3. The 2- NH_2 influences the H in position 1 far more than that in position 6, and the latter more than in 3. The action of Sn and HCl on both the 1,6-Br and the 1,3,6-Br derivs. removes the Br in position 1 the most readily. In this case again the NH_2 influences the substituent in position 1 far more than in 3 and 6. The following derivatives of A were prepd.: 6-bromo hydrochloride, by reduction of the 1,6-Br deriv. with Sn + HCl, SnCl_2 + HCl, HI, or CuCl + HCl; needles, darkens 200° , m. 267° ; 6-bromo-2-acetyl, microcrystals from alc., m. 192° ; 6-bromo-2-benzoyl, leaves from alc., m. 218° ; 3,6-dibromo, from the 1,3,6-Br deriv. and Sn + HCl, small leaves from alc., m. 187° ; 3,6-dibromo-2-acetyl, long needles from alc., m. 195° ; 3,6-dibromo-2-benzoyl, long lustrous needles, m. $161-2^\circ$.

D. BRÉSE JONES

Synthesis of *m*-dihydroxybenzaldehyde. F. MAUTHNER. Univ. Budapest. *J. prakt. Chem.* 101, 93-6 (1920).—Dicarbomethoxy-*m*-dihydroxybenzaldehyde, obtained in 80% yield by reducing the corresponding BrCl deriv. by means of Pd-BaSO₄ and H₂, crystals from C₆H₆, m. $154-5^\circ$; *p*-nitrophenylhydrazone, red needles from alc. m. $223-3^\circ$. The MeO deriv. was converted into *m*-dihydroxybenzaldehyde by slowly adding 7 g. of the former in 10 cc. alc. to 56 cc. 2 N NaOH and allowing the mixt. to stand for 45 mins. at room temp., the reaction being carried on in H₂. After cooling, 60 cc. 2 N H₂SO₄ was added, the soln. concd. *in vacuo* to about a third of its vol. at not over 50° , then extd. with Et₂O, and the product dissolved in AcOEt and pptd. with ligroin; needles, m. $145-6^\circ$. It gives a reddish violet color with concd. H₂SO₄. *p*-Nitrophenylhydrazone, crystals from 50% AcOH, chars without m. 280° ; semicarbazone, needles from H₂O, m. $223-4^\circ$ (decompn.).

D. BRÉSE JONES

The determination of active hydrogen in organic compounds. R. CUSA. Univ. Bologna. *Gazz. chim. ital.* 50, II, 53-5 (1920).—Moureu and Mignonac (*C. A.* 8, 3008) proposed a method for differentiating amines based on their behavior with EtMgBr . The test was made at 40° in Et₂O, using a great excess of EtMgBr in Et₂O and measuring the C₂H₆ formed over H₂O, which dissolved the Et₂O that passed the condenser. Other solvents were used by Hibbert (*C. A.* 6, 1744) and Zerevitinov (*C. A.* 5, 1285; 6, 203). Z. also applied it to alcs., sugars, acids, phenols, oximes, flavonols, thiophenols, imides and amides and obtained concordant numbers. The diamides (urea, thiourea, phenylurea, menthone semicarbazone) give an active H atom less than calcd. The compds. like $\text{AcCH}_2\text{CO}_2\text{Et}$ behave as though composed entirely of the enol form. B. Oddo (*C. A.* 5, 3423) obtained better results than Z. C. had occasion to det. the active H in some compds. and selected the method of M. and M. because of the simple app. required and used Et₂O as solvent because of its accessibility. The results together with those of M. and M. show the method to be accurate. The data are given in a table as cc. C₂H₆ obtained and calcd. and as active H obtained and calcd. In the following the active H obtained follows the compd.: MeOH 1.05, PhOH 1.04, resorcinol 2.01, α -naphthol 1.11, pyrrole 1, α -methylindole 1.07, *N*-methylpyrrole 0, *N*-methylindole 0, PhCH:NNHPh 1.16, $\text{AcCH}_2\text{CO}_2\text{Et}$ 1.03 and 1.06, $\text{AcCHEtCO}_2\text{Et}$ 1.04 and 1.63, MeNO₂ 0.87 (calcd. 0.83), EtNO₂ 0.95 (calcd. 0.65), C₆H₅(NO₂)₂ 0.

E. J. WITZEMANN

Separation of α -naphthylphenylaminomethane into its optical antipodes. S. BERLINGOZZI. Univ. Siena. *Gazz. chim. ital.* 50, II, 56-9 (1920).—B. has previously shown (*C. A.* 14, 3410; 15, 68) how either by reduction of α -naphthylphenylketone or by the action of α -C₁₀H₇MgBr on hydrobenzamide α -naphthylphenylaminomethane (A), m. $56-9^\circ$ is obtained. The formula contains an asym. C atom and the compd. should exist in 2 optical isomers. 8 g. A in 500 cc. 95% EtOH were mixed in the cold with 5.5 g. tartaric acid in 50 cc. EtOH. Shining white crystals began to sep. almost

at once and after 18 hrs. 12.6 g. were obtained. This product was extd. with boiling alc. and left 5.5 g. of a less sol. tartrate. The alc. solns. on cooling sepd. 4.1 g. of mixed tartrates. The little sol. tartrate is quite sol. in boiling H_2O , from which it crysts. in white scales that m. 190–207° (decompn.). 4 g. of this tartrate was dissolved in a small excess of NaOH and the soln. extd. with Et_2O . The product, m. 81–2°, showed $[\alpha]_D^{15}$ 63.61° and was the *d*-isomer of A. The more sol. fraction of the tartrate sepd. as white needles, m. 195–210° (decompn.). Treated with NaOH it gave the *l*-isomer of A, m. 81–2°, $[\alpha]_D^{15}$ –63.38°. The hydrochloride of the *d*-form, obtained by dissolving it in warm 1.0 N HCl, needles, m. 275–80° (decompn.), $[\alpha]_D^{15}$ –53.43°. The hydrochloride of the *l*-form seps. as silky white needles, m. 275–80°, $[\alpha]_D^{15}$ 53.18°.

E. J. WITZEMANN

The synthesis of sulfuryl chloride in the presence of organic compounds. G. CUSMANO. Florence. *Gazz. chim. ital.* 50, II, 70–80(1920).—It has long been known that HCO_2H , $AcOH$, C_2H_4 and camphor favor the reaction $SO_2 + Cl_2 \rightarrow SO_2Cl_2$, which without them proceeds slowly in sunlight. The C_2H_4 is chlorinated during the reaction and when this is complete SO_2Cl_2 ceases to be formed. HCO_2H and $AcOH$ are also altered in the reaction but without definite relation to the production of SO_2Cl_2 . Camphor is not changed in the reaction. In previous work C. (C. A. 13, 1587) found that other compds. have the same effect. In extending this investigation C. has tested some other compds. and first detd. the influence of the CO group of camphor. Thus dihydrocamphorone, cyclohexanone, tetrahydrocarvone, menthone and fenchone were tested; all of them behave like camphor. When their halogen derivs. are used they lose this property. Of the terpenic ketones, carvone, pulegone, and carvotanacetone were tested and found to favor the synthesis of SO_2Cl_2 . These compds. contain both an unsatd. linking and a CO group. C.'s expts. have convinced him that of these the CO group is more active than the ethylene double bond. $AcMe$ does not promote the reaction, probably because it is so rapidly chlorinated. This chlorination is so much diminished at –60° that $AcMe$ now promotes the reaction. $MeCOEt$ behaves similarly while Me nonyl ketone is catalytically active even at –10°. $AcPh$ catalyzes the reaction at –10° but is chlorinated. $BzPh$ and fluorenone catalyze the reaction without being chlorinated but lose the power to do so if previously brominated or nitrated. The monocarbonyl ketones accordingly have the property in general of increasing the velocity of combination of Cl with SO_2 and lose this property when halogens, NO_2 or SO_2H groups are introduced at any distance from the CO (as tested with α -, β - and γ -monobromocamphor). The presence of CO_2H does not interfere. The influence of the chain bound to the CO does not appear to be great. The 1st interpretation of the reaction offered and tested is that these compds. act through the basic property of their oxygen, i. e., by the formation of unstable oxonium salts with the Cl or SO_2 or both, and these salts are not formed when a negative atom or group is introduced, because this basicity is neutralized. In order to test this hypothesis various other compds. were tested. Cineole, which favors the reaction, undergoes chlorination as the Et ester, which had to be used at –45–50° in order to give good results. Since the formation of oxonium derivs. is characteristic of O compds. aldehydes, acids and esters were tried. Alcs. were excluded because of their ease of chlorination. $EtCHO$ gave good results at –50°. BzH and piperonylic aldehyde even at –10° did not catalyze the reaction well. Meta- and paraldehyde gave fair results at –10°. $AcOH$ and $BzOH$ promote the reaction at –10° slowly. $BzOH$ is not chlorinated and is therefore the best. $AcOEt$ and $BzOEt$ act, but must be protected from the Cl by working at –50°. Of other compds. containing two O functions used, ketocineole and camphorcarboxylic acid promote the synthesis, while camphorquinone, buccocamphor, benzo- and thymoquinone are inert at –10°. In the α,α -diketones the one CO acts as a negative group toward the other and if one is converted into an oxime the

compd. becomes catalytically active; isonitrosocamphor acts like camphor. With the quinones the inactivity is probably due to the formation of relatively stable addition products with Cl or SO₂. The inactivity of dibenzalacetone and similar compds. may be explained analogously. The results are summarized in a large table. The compds. were used in equimol. amts., treated with excess of SO₂, reduced to a detd. temp. and treated for the same period of time at the same rate with SO₂ and Cl₂ dried with H₂SO₄. The SO₂ was expelled and the SO₂Cl₂ removed and detd. by distn., after which the residue was examd. In only a few cases was the compd. used for catalysis recovered unchanged. In most cases it was chlorinated. Blank expts. showed whether this was due to the Cl or SO₂Cl₂ either during the synthesis or distn. C. thinks that a transitory compd. is formed of the oxonium type, but that not all compds. capable of giving these derivs. necessarily favor the reaction but only those that are formed and decompd. with a certain velocity. The ketones and esters seem to have the required properties in the right degree. The expts. are being continued.

E. J. WITZEMANN

The binary equilibria of some nitro derivatives of toluene. M. GUA. Univ. Sassari. *Gazz. chim. ital.* 50, II, 101-13(1920).—G. has previously studied the binary systems of various NO₂ derivs. of PhMe that are present in drain oil (olio di sgocciolamento) obtained as a by-product in the manuf. of *m*-(O₂N)₂C₆H₃Me. Bell and Herty (C. A. 14, 347) have corrected G.'s data by extrapolation. This is not justified according to G. and he has repeated the main expts. and discusses the matter in detail. While G.'s reply was in press the paper of Wogrinz and Vári (C. A. 14, 3530) was received, in which his own views and results were confirmed.

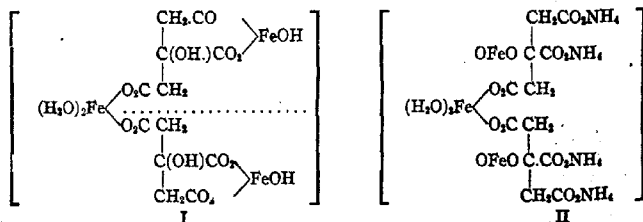
E. J. WITZEMANN

Electrolytic reduction of the hydroxyazo compounds. II. E. PUXEDDU. Univ. Cagliari. *Gazz. chim. ital.* 50, II, 149-59(1920).—In a previous paper (C. A. 13, 843) P. has given an account of the electrolytic reduction of *p*-hydroxyazobenzene in HCl-EtOH and AcOH-H₂SO₄. Hausermann reduced PhNO₂ in alk. and acid solns. (*Chem.-Ztg.* 17, 125, 206(1893)) with the elec. current and obtained the hydrazo compd. in the former and benzidine and azoxybenzene in the latter. Elbs (*Chem.-Ztg.* 17, 206(1893)), using other cathode material, obtained different results. Gattermann (*Ber.* 26, 1844, 2810(1893); 27, 1927(1894)) obtained aminophenols by electrolytic reduction. Other expts. by Löb (*Z. Elektrochem.* 7, 337, 577(1900)) showed that the best results are obtained by using unattackable electrodes. In continuing his expts. P. has modified the app. previously used by putting a 2-hole stopper in the porous vessel containing the cathode liquid. Through the one hole the cathode wire was passed with an open glass tube. To the other a reflux condenser was attached so that the solvent might be boiled. This change was necessary to prevent rapid evapn. of the cathode liquid. *p*-Hydroxyazobenzene, *o*- and *p*-tolueneazophenol, benzeneazo-*o*-cresol, benzeneazo-*p*-cresol and the benzeneazo compd. of salicylic acid were studied. The N compd. was dissolved in 95% EtOH and HCl or H₂SO₄ with H₂O. The decoloration of the cathode liquor was taken as the end-point. The EtOH was evapd. and the salts of the PhNH₂ deriv. and the H₂NC₆H₄OH deriv. sepd. by crystn. or treated at once with Na₂CO₃. Aq. solns. in NaOH were also electrolyzed from which the PhNH₂ deriv. only could be sepd. A c. d. of 1.5-2 amps. gave the best results. With H₂SO₄ a Pb cathode was used. In all cases the reduction gave similar results. Two bases were always formed. One is the PhNH₂ deriv. used in the copulation to obtain the hydroxyazo compd. The other is the aminophenol corresponding to the phenol used in the same copulation. The *p*- and *o*-hydroxyazo compds. behave in electrolytic reduction in the same way that they do toward other reduction processes. No other products of reduction could be found in the electrolytic reduction of these compds. The exptl. details for each of the substances reduced are given.

E. J. WITZEMANN

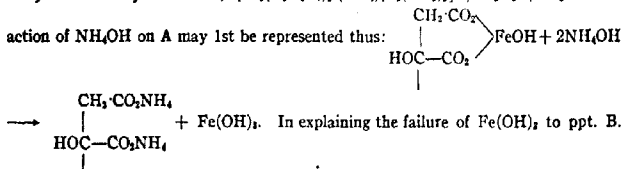
The organic salts of iron. II. Ferric citrates and ferric ammonium citrates. R. BRILLONI. Milan. *Gazz. chim. ital.* 50, II, 159-212(1920).—In recent years much

has been done toward clarifying the structure of org. salts of Fe by the application of Werner's theory of coordination. Such studies have been made of the formates, acetates, benzoates and salicylates of Fe which are reviewed in the first 10 pages of this paper. This is followed by 8 pages of a chronological review of the Fe citrates. Ferric citrate was believed to be a normal salt until Martinotti and Cornelio (*Boll. chim. farm.* 40, 455, 481, 549(1901)) pointed out its strange chem. behavior from this point of view. The accepted simple chemistry of the green and red NH_4Fe citrates was also questioned by M. and C. who, proposed some new formulas. Siboni (*Boll. chim. farm.* 1905, 625) wished to explain their structure by assuming that Fe is tetravalent. Gerock (*C. A.* 2, 2425) thought that the Fe entered as a metalorganic acid radical. *I. Ferric citrate.* In all cases the existence of a normal Fe salt was the basis of the various hypotheses concerning the structure of the citrates. The Fe of these salts however is not pptd. by NH_4OH nor by $\text{K}_4\text{Fe}(\text{CN})_6$, which suggests the idea that Fe is contained in a complex ion. B. tried first to obtain the normal citrate ($\text{C}_6\text{H}_5\text{O}_7\text{Fe}$) by dissolving $\text{Fe}(\text{OH})_3$ in citric acid and obtained a perfectly limpid soln. but all attempts to cryst. out a salt failed. On drying over concd. H_2SO_4 only the amorphous salt as scales, or as a red-brown mass having a chonchoidal fracture, was obtained. This material contained Fe and citric acid in the proportion used. When some of this material was concd. to a sirupy consistency and pptd. with excess EtOH red-yellow Fe citrate was sepd., which sepd. from H_2O at 50° as fine laminas. The compn. of this material corresponds to $[\text{Fe}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{OH})_2] \cdot 1/3\text{C}_6\text{H}_5\text{O}_7 \cdot 8\text{H}_2\text{O}$ and is identical in structure with the formates, etc., of Fe referred to above. Of the 8 mols. of H_2O 6 are eliminated at 100° . The other 2 are removed only by prolonged drying at 120° and may be considered to be united to the central nucleus. When mol. amts. of $\text{Fe}(\text{OH})_3$ and citric acid react 2/9 of the citric acid remains free thus: $9\text{Fe}(\text{OH})_3 + 9\text{C}_6\text{H}_5\text{O}_7 \rightarrow \text{Fe}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{OH})_4 + 2\text{C}_6\text{H}_5\text{O}_7 + 21\text{H}_2\text{O}$. Similarly in the reaction $9\text{FeCl}_3 + 9\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 + 6\text{H}_2\text{O} \rightarrow \text{Fe}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{OH})_4 + 27\text{NaCl} + 2\text{C}_6\text{H}_5\text{O}_7$ it was found that 2/9 of the citric acid was liberated. Consequently the ordinary Fe citrate is *dicitratotetriferric citrate*, i. e., is the citrate of the base $[\text{Fe}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{OH})_2]\text{OH}$, from which it should be possible to obtain other salts of org. acids. Thus the *chloroplatinate*, $[\text{Fe}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{OH})_2] \cdot 1/2\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$ was obtained. The formation of this salt confirms the fact that in Fe citrate only 1/7 of the citrate is ionizable and substitutable by other acid radicals. The remaining citrate groups form a relatively stable complex radical with the Fe. These views conform with the chem. behavior of the salt, which reacts for the dicitratetetriferric ion and not for Fe^{++} unless the complex is broken down with strong reagents. In the Fe citrate soln. the hydrolytic dissociation may be quite complete so that it is not possible to obtain the trisilver citrate by pptg. with AgNO_3 unless the soln. is first accurately neutralized with NH_4OH . On the basis of its analogy to Fe formate (Belloni, *C. A.* 3, 1503) and to the ferric and ferrichromic acetates (Weinland and Herz, *C. A.* 8, 61) B. has assigned the structure I to this complex ion. This salt differs from the acetates mentioned in being an internal complex salt such as those of benzhydrox-

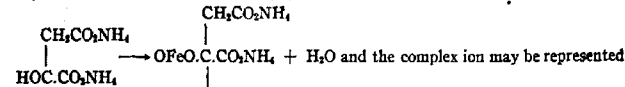


amic acid (Werner, Matisen, C. A. 12, 1883. B.'s final conclusion is that the Fe citrate dried at 100° is *diaguo-dicitratodioltriferric citrate* (A), $C_6H_5O_7[Fe(C_6H_5O_7Fe(OH)_2(OH_2)_2)]_3$. B. was interested to see if the Cr citrate which has not been described could be prepd. Freshly pptd. $Cr(OH)_3$ with an equimol. amt. of citric acid gives Cr citrate as scales, dark blue by reflected and violet by transmitted light. Its solns. give evidence of dichroism and fail to react for Cr^{++} ions. With NH_4OH the soln. becomes green and nothing is pptd. with alkalis, from which it appears that the complex Cr base is more stable than that of Fe above. This product is the *diaguo-dicitratodioltrichromic citrate*, $[Cr_2(C_6H_5O_7)_2(OH)_2(OH_2)_2] \cdot 1/3 C_6H_5O_7 \cdot 4H_2O$. From this citrate the *chloroplatinate* $[Cr_2(C_6H_5O_7)_2(OH)_2(OH_2)_2] \cdot 1/2 PtCl_6 \cdot 3H_2O$ was obtained. The existence of a mixed *dicitratodichromiferric base* was put in evidence by the compd. $[FeCr_2(C_6H_5O_7)_2(OH)_2] \cdot 1/3 C_6H_5O_7 \cdot 6H_2O$. II. *Red ammonium ferric citrate*. This citrate is formed by the addition of NH_4OH to the solns. of A. If 7 mols. alkali are added to a soln. of $A Fe(OH)_3$ is pptd. When NH_4OH to the extent of 4 mols. is added drop by drop a red neutral soln. is obtained and no pptn. occurs on adding excess. If likewise 4 mols. of $NaOH$ or KOH are added the soln. becomes red and remains neutral. From this it is concluded that the Fe citrate complex ion can absorb 4 mols. of alkali without breaking up. The NH_4 deriv. obtained by evapg. on the H_2O bath had the compn. $[Fe_3(C_6H_5O_7)_7(NH_4)_4O_7] \cdot 1/3 C_6H_5O_7 \cdot 4H_2O$ and since dried at 120° it loses 2 H_2O it is a *diaguo-dicitratodioxytetramminoferric citrate*, $[Fe_3(C_6H_5O_7)_7(NH_4)_4O_7(OH_2)_2] \cdot 1/3 C_6H_5O_7 \cdot 2H_2O$. The

action of NH_4OH on A may 1st be represented thus:



In explaining the failure of $Fe(OH)_3$ to ppt. B. departs from previous ideas based on the acid function of OH in glycols, glycerol, etc., and assumes that the acid is FeO_3H , which esterifies the citric acid thus: $HOFeO + CH_3CO_2NH_4$



and the complex ion may be represented by II. The salt is *diaguo-disferrylcitratetetramminoferric citrate* (B), $C_6H_5O_7[Fe(C_6H_5O_7Fe(OH)_2(NH_4)_2(OH_2)_2)]_2 \cdot 6H_2O$. When but 2 mols. of NH_4OH are added *diaguo-citratoferrylcitratodiammino-ol-ferric citrate* (C), $C_6H_5O_7[Fe(C_6H_5O_7Fe(OH)(NH_4)(OH_2)_2)]_2 \cdot 6H_2O$, is formed. The *chloroplatinales* of the bases in B and C were both obtained and analyzed. The solns. of B can dissolve excess of $Fe(OH)_3$ to the extent of 6.86 mols. $Fe(OH)_3$ in addition to the 3 atoms Fe already present. III. *Green ammonium ferric citrate*. The various hypotheses concerning the constitution of this green form depend upon wrong facts concerning the components. If equal vols. of 3 N tri-Na citrate and $FeCl_3$ are mixed the red-brown color changes to green when 1.5 vols. of the former are present with 1 vol. of the latter. The soln. now contains the green Na ferric citrate and $NaCl$. After dialysis this soln. seps. scales (or by adding $BtOH$) of trisodium ferricitrate (D) $Fe_3(C_6H_5O_7)_7Na_3H_2$ which does not give reactions of Fe^{++} . Its solns. are distinctly acid. All but the Na and H constituents a hexavalent complex ion of which the salt is the tri-Na salt. Two mols. $Fe(OH)_3$ treated with 3 mols. citric acid give free *ferricitric acid*, which with 3 mols. $NaOH$ gives D or with NH_4OH gives *triammonium ferricitrate* used in pharmacy. The hexavalence of ferricitric acid should it seems give rise to six NH_4 salts, depending on the amt. of

NH₄OH added. Salts with more than 3 NH₄ are not obtained, the extra NH₄OH evaps. off. In this respect it resembles citric acid, which combines with not more than 2 NH₄ groups. B. concludes, therefore, that 1 CO₂H is attached to Fe and this leaves but 1 CO₂H in each citric acid mol. to combine with NH₄. The absence of H₂O of crystn. leads him to conclude that coördinating valences of the 2 Fe atoms are recipro-

cally satd. This leads him to the structure $\left[\text{Fe}_2 \left(\begin{array}{c} \text{O}_2\text{C} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \right) \text{C}_2\text{H}_4 \left(\begin{array}{c} \text{CO}_2 \\ \diagdown \quad \diagup \\ \text{CO}_2 \end{array} \right) \dots \right]^{++++}$ for this complex ion. The mono-, di- and triammonium ferricitrates are described.

E. J. WITZEMANN

Interchangeability of ester and alcohol groups in the presence of catalyzers. EMIL FISCHER. Univ. Berlin. *Ber.* 53B, 1634-44(1920).—The reaction studied by Purdie (*J. Chem. Soc.* 53, 391(1887)) seems to be general, i. e., between every alc. and every ester grouping there occurs an interchange of the acid radical at relatively low temps., in the presence of a suitable catalyzer, until an equil. is established; with the polyvalent alcs. the process naturally becomes more complicated. Thus, when 2 g. HOCH₂CH₂OBz (A) is heated on the H₂O bath in 20 cc. CHCl₃ with 1.5 g. freshly ignited K₂CO₃, filtered after 24 hrs., evapd. and kept *in vacuo* over P₂O₅, 0.5 g. of the fine needles of (CH₂OBz)₂ (B) cryst. out; conversely from 13.5 g. B and 3.1 g. glycol boiled 20 hrs. under a reflux in 30 cc. CHCl₃ with 8 g. K₂CO₃ are obtained 1.4 g. glycol, 5.7 g. B and 5 g. A. Again 6.0 g. B refluxed 15 hrs. in 12 cc. abs. EtOH with 0.5 g. K₂CO₃ yields 1.0 g. BzOK, 3.8 g. BzOEt and 0.5 g. A + B, and 6.0 g. B, 15 cc. MeOH and 2.5 cc. of 6.5% NaOMe in MeOH under the same conditions give 5.6 g. BzOMe, traces of A and 0.3 g. B, while from 3.1 g. glycol, 6.8 g. BzOMe, 0.3 g. K₂CO₃ and 30 cc. CHCl₃ refluxed 20 hrs. are obtained 4.4 g. BzOMe, 1.8 g. A and 0.6 g. B; with 3 instead of 0.3 g. K₂CO₃, the yields of the 3 products are 3.4, 1.0 and 1.0 g., resp. *m*-HOC₆H₄OBz (3 g.) refluxed 14 hrs. in 25 cc. CHCl₃ yields C₆H₄(OH)₂ and 0.9 g. C₆H₄(OBz)₂; 3 g. of this with 1 g. *m*-C₆H₄(OH)₂ and 0.2 g. K₂CO₃ refluxed 16 hrs. in 10 cc. each of Et₂O and CHCl₃ gives 1 g. *m*-BzOC₆H₄OH. From 6.5 g. monoacetin in 40 cc. CHCl₃ shaken 14 hrs. with 4 g. K₂CO₃ is obtained 2.6 g. of an oil, *b*₁₀, 110°, consisting chiefly of diacetin. Glycerol (9.2 g.) and 13.6 g. BzOMe in 15 cc. C₆H₅N heated 20 hrs. on the H₂O bath with 0.82 cc. of 6.5% NaOMe give 7 g. benzoylglycerols; with 0.54 g. solid NaOMe instead of a MeOH soln., 8.5 g. From 4.6 g. glycerol and 7.6 g. *o*-HOC₆H₄CO₂Me in 8 cc. C₆H₅N heated 10 hrs. on the H₂O bath with 0.5 g. NaOMe are obtained 3.5 g. glycerolsalicylins; 4 g. acetoneglycerol boiled 22 hrs. with 4 g. BzOMe and 0.25 cc. of 6.5% NaOMe gives 3.3 g. BzOMe + acetoneglycerol and 1.3 g. benzoylacetoneglycerol; 0.9 g. glycerol, 0.1 g. NaOEt and 4 g. tribenzoin kept 3 days at room temp. in 15 cc. C₆H₅N yield 0.6 g. mono- and 3.5 g. dibenzoylglycerol; from 6.8 g. BzOMe and 7.5 g. PhCH₂OAc refluxed 20 hrs. in 50 cc. CHCl₃ with 0.4 cc. of 6.5% NaOMe are obtained 11.1 g. BzOMe + PhCH₂OAc and 1.8 g. PhCH₂OBz; with 0.82 cc. of NaOMe after 20 hrs. boiling, 7.2 g. of the original esters and 3.0 g. PhCH₂OBz; with 0.82 cc. NaOMe after 9 days at room temp., 3.3 g. PhCH₂OBz; with 0.5 g. solid NaOMe after 12 hrs. on the H₂O bath, 5.6 g. PhCH₂OBz. In the course of this work the following derivs. of trimethyleneglycol (C) were prepd.: *Monobenzoate* (5 g. from 7.6 g. C and 6.5 g. quinoline slowly treated at 0° with 7.0 g. BzCl and allowed to stand 24 hrs. at room temp.), is a relatively mobile oil, *b*₁₁ 163-4°, sol. to the extent of about 1% in cold H₂O; at the same time there is formed 2.7 g. of the dibenzoate, m. 59°. From 7.6 g. C and 6.5 g. quinoline with 9.3 g. *p*-O₂NC₆H₄COCl in 25 cc. CHCl₃ are obtained 3 g. of the *di-p*-nitrobenzoate, long needles from alc., m. 120°, and 7 g. of the *mono-p*-nitrobenzoate, faintly yellow oil, *b*₁₀, 166-8°, long needles from Et₂O-petr. ether, m. 49°.

C. A. R.

Preparation of β-tetrahydronaphthyl methyl ketone. ALBERT R. F. HIGGS. I. and W. Hochschule Berlin. *Ber.* 53B, 1645(1920).—The suggestion of v. Braun

(C. A. 14, 3659) that the extraordinary energy with which AcCl reacts with tetrahydronaphthalene (A) as observed by Scharwin (*Ber.* 35, 2511(1902)) might have been due to the presence of dihydronaphthalene in the A has been confirmed. If A prepd. catalytically from C_{10}H_8 and free from lower hydrogenated products (Tetralin-G.-m.-b.-H.) and AcCl are treated in CS_2 with AlCl_3 reaction sets in very gently and without resinification, and on proceeding further as recently described for hydrindene (v. B., *loc. cit.*) β -tetrahydronaphthyl Me ketone is obtained on the first fractionation in almost 90% yield as a clear, only slightly yellow oil b_{10} 182° ; semicarbasone, m. $234-5^\circ$.

CHAS. A. ROULLER

Action of aluminium chloride on solutions of aromatic nitrohydrocarbons in aromatic hydrocarbons. A. KLEGL AND HANS HUBER. Univ. Tübingen. *Ber.* 53B, 1646-55(1920); cf. Freund, *Monatsh.* 17, 399(1896).—When 300 g. PhNO_2 and 1200 g. PhMe on the H_2O bath are treated in the course of 8 hrs. with 400 g. AlCl_3 , poured into ice H_2O , sepd. from the PhMe layer, freed from the PhMe and unchanged PhNO_2 with steam and filtered hot and the HCl salt which seps. in silvery leaflets is treated in hot H_2O with NH_4OH , and the dark violet ppt. is dried in Et_2O and distd. *in vacuo* there is obtained 16 g. *p*-aminophenyl-*p*-tolyl (A), b_{11} about 190° , crystals from ligroin, m. 99° ; acetyl derivative (3.2 g. from 3 g. A boiled a short time with 12 cc. Ac_2O), scales from AcOH , m. 221° . The tarry H_2O -insol. portion of the condensation product, when gradually heated to 180° with superheated steam, yielded 2.5 g. of a brownish distillate solidifying quite rapidly and sepg. from benzine in the fine needles, m. $88-9^\circ$, of *p*- $\text{MeC}_6\text{H}_4\text{NHPh}$ (B). K. and H. believe that in the condensation the PhNO_2 is reduced to PhNH_2 , which with the PhMe forms B and also, at the instant when it rearranges into *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{OH}$ (C), *i. e.*, when the latter is in the "nascent" state, forms A with the PhMe. As a matter of fact, from 15 g. PhNH_2 , 300 g. PhMe and 50 g. AlCl_3 allowed to stand 2 days with frequent shaking are obtained 1.2 g. B and 2 g. A. HCl, but preformed C does not condense with PhMe in the presence of AlCl_3 . The HCl salt of 5 g. A in 400 cc. H_2O and 10 cc. concd. HCl diazotized in ice with 2 g. NaNO_2 in 20 cc. H_2O and, when all has dissolved, heated 2 hrs. on the H_2O bath yields 4.6 g. *p*-hydroxyphenyl-*p*-tolyl, silvery leaflets from 50% AcOH , m. $154-5^\circ$, also obtained by Hirsch's method (shaking diazotized *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$ with PhOH ; Ger. pat. 58,001); benzoid, obtained quant. by the Schotten-Baumann method, leaflets from AcOH , m. 188° . In prep. *p*-hydroxyphenyl-*o*-tolyl (D) from *o*- $\text{MeC}_6\text{H}_4\text{NH}_2$ by H.'s method, the alk.-sol. portion of the product proved not to be homogeneous; on distn. *in vacuo* it yielded within 30° 3 fractions (60, 25 and 15%) the last two of which at once yielded solid benzoates while the first gave a tarry mass which could be made to cryst. only after repeated treatment with alc. The solid benzoates from all these fractions were identical, sepg. from alc. in needles, m. 89° , also obtained by diazotizing Bamberger's "*p*-aminophenyl-*p*-tolyl" (prepd. by reduction of a $\text{O}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{Me}$ which he obtained from *p*-nitroisodiazobenzene and PhMe (*Ber.* 28, 405(1895)); also made by Kühling by the action of acid chlorides and PhMe on Na *p*-nitrophenylnitrosamine (*Ber.* 28, 43(1895)) and benzoylating the dark oil resulting from the decompn. of the diazo compd. The free D, obtained in 2.5-g. yield from 4.1 g. of the benzoate in 15 cc. alc. warmed with 0.71 g. Na in 25 cc. alc. until the Na compd. of D sepd., then at once treated with H_2O until the ppt. redissolved, freed from most of the alc. by heating and pptd. with CO_2 , long needles from ligroin, m. $84-5^\circ$. From the above facts, further strengthened by the observation that reduction of the $\text{O}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{Me}$ obtained by Carnelly by nitration of *p*- $\text{MeC}_6\text{H}_4\text{Ph}$ (E) (*Jahresb.* 1876, 419) gives a product identical with A, K. and H. believe that B.'s and K.'s $\text{O}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{Me}$ and the products derived from it (nitro- and aminophenylbenzoic acids, amino- and acetaminophenyltolyl) are *o*- and not *p*-tolyl derivs. The E, leaflets from MeOH, m. $49-50^\circ$, was obtained in 14-g. yield from 60 g. *p*- $\text{MeC}_6\text{H}_4\text{N(NO)Ac}$ slowly added to C_6H_6 and after 1 day freed from C_6H_6 ,

with steam (finally at 130–40°), again taken up in C_6H_6 and shaken with concd. H_2SO_4 to remove impurities. 3,4'-Dimethyl-4-aminobiphenyl (obtained like A in 18-g. yield from 300 g. o -ONC₆H₄Me and PhMe), m. 42–3°; acetyl derivative, needles from alc., m. 206°.

CHAS. A. RÖHLER

Hydrogenation of furfuralcohol (2-furancarbinol) and of furfural to tetrahydrofurfuralcohol (tetrahydro-2-furancarbinol). HEINRICH WIENHAUS. Univ. Göttingen. Ber. 53B, 1656–66(1920).—2-Furancarbinol (A) (0.5 g.), prepd. from furfural (B) by means of NaOH and freed from B with $H_2NCONHNH_2$ and subsequent steam distn. so that it does not redden $PhNH_2$.AcOH paper in the least, when shaken with 0.05 g. Paal Pd in 15 cc. H_2O satd. with H absorbs 4 atoms H in 225 min. In another expt. 24.5 g. A with 10 cc. of 4% $PdCl_2$, a little gum arabic and NaOH to neutralize the HCl set free from the $PdCl_2$ absorbed 4 atoms H in 170 hrs. (5 cc. fresh $PdCl_2$ having been added after 20, 52, 76, 98 and 140 hrs.). The A can also be hydrogenated without using a diluent; thus 24.5 g. absorbed 3 l. H_2 in 5 hrs. when shaken with Pd charcoal (Mannich and Thiele, C. A. 10, 2158), but after this it was necessary repeatedly to add fresh catalyzer suspended in Et_2O , the latter being removed by evacuating the vessel; from the first a little calcined soda was added and after the satn. was complete the tetrahydro-2-furancarbinol (C) was simply drawn off from the catalyzer and distd. This last method of hydrogenation is to be recommended, as C cannot be sepd. from H_2O by the usual methods. Despite repeated shakings of the aq. filtrate from the Pd only a fraction of the C (about 0.1) goes into Et_2O , and likewise the greater portion remains behind in the flask when a part of the H_2O is distd. off, making it very probable that C forms a hydrate. It can be removed fairly completely from H_2O only when the liquid is satd. with potash; the alc. layer, even after long contact with fused potash, always yields on distn. a first fraction of H_2O , then a fraction b. 170–95° and leaves about 12% of a residue of high boiling polymerization products. By fractionation *in vacuo*, the C can be obtained pure; it b_{24} 85–6°, b_{740} 177°, d_{20}^{20} 1.054, n 1.44933, 1.45167, 1.45680, 1.46138 for α , D, β and γ at 20°, E_D —0.17, —0.16, —0.16, —0.17, 0.01, 0.00 for α , D, β , γ , β — α and γ — α . A b_{21} 80°, b_{24} 82–3°, b_{46} 96°, b_{740} 171°, d_{20}^{20} 1.131, n 1.48108, 1.48477, 1.49398, 1.50192, E_D —0.44, —0.45, —0.43, —0.43, 0.00, 0.01. C does not decolorize Br in H_2O or petr. ether, does not rapidly reduce very dil. $KMnO_4$, does not color a pine splinter moistened with concd. HCl, while A at once decolorizes Br water, changes Br in petr. ether in 1 sec. to violet and in the course of some days deposits a gleaming layer of carbon, quickly reduces $KMnO_4$ and gives a vivid blue-green color with a pine splinter moistened with HCl. Both A and C absorb moisture from the air. C heated 2 hrs. on the H_2O bath with 2 parts freshly distd. $AcCO_2H$ yields the pyruvate, b_{17} 110–30°, which with $H_2NCONHNH_2$ gives the semicarbazone, $H_2NCONHNH:CMcCO_2CH_2C_6H_5O$, white leaflets, m. 184–6°, insol. in soda. A, on the other hand, with $AcCO_2H$ immediately turns green, evolves much heat and, in spite of cooling, gives in 1–2 min. a pure deep dark green elastic mass. Phenylurethan of C, from 0.5 g. each of $PhNCO$ and C allowed to stand overnight in 1–2 cc. C_6H_6 , flat briquet-shaped crystals from petr. ether, m. 61°. Phenylurethan of A, needles, m. 45°. Diphenylurethan of C, from 4.6 g. Ph_2NCOCl , 2.0 g. C and 3 g. C_6H_5N heated 1 hr. on the H_2O bath, tablets from MeOH, m. 81°. Attempts to hydrogenate B by the Paal or Skita method showed that not only the 2 ethylene linkages but the aldehyde grouping also are reduced; good results were obtained by working without a solvent. Thoroughly purified charcoal suspended in $PdCl_2$ soln. was satd. with H, filtered with suction (without allowing it to go dry in the air), washed with alc. and Et_2O and kept under Et_2O ; a part of this was introduced into the hydrogenation app. with 48 g. B, the Et_2O removed *in vacuo* and the app. filled with H_2 ; on shaking, 8 l. H_2 was absorbed in 7 hrs, 9 l. in 15 hrs.; fresh catalyzer was introduced 10 times, somewhat more than 6 atoms H finally being absorbed in 235 hrs. The resulting brown oil (48 g.) on repeated distn. gave at least 0.5 of its wt. of a frac-

tion consisting undoubtedly of C, some H₂O and higher boiling fractions decreasing in amt. but increasing in C content and viscosity with the temp. CHAS. A. ROUILLER

Organic disulfides. FRITZ v. KONEK. Univ. und Techn. Lab. Chem. Zentr.-Versuchsstat. Budapest. *Ber.* 53B, 1666-71(1920); cf. Lecher, *C. A.* 14, 3078.—Thirteen yrs. ago v. K. found (*Verh. deutsch. Naturf. und Ärzte, Köln.* 1908, Part II) that antipyril disulfide (smoothly obtained from antipyrine and S₂Cl₂) when shaken with Hg in CHCl₃ does not lose S but adds an atom of Hg, yielding a well crystd. compd. designated as mercuriodithiobisantipyrine; he concluded that the substance was a mercaptide of thioantipyrine, Hg(SA)₂, or a Hg addition product, A₂S:SHg; an interpretation in the sense of the modern theory of dissociation into radicals could not have been expected at that time. To det. whether this reaction was peculiar to antipyril disulfide or general for org. disulfides, other disulfides were tried. Et₃Sn, (Me₂NC₆H₄)₂S₂, (PhCH₂)₂S₂, Bz₂S₂ and (p-O₂NC₆H₄)₂S₂ did not add a trace of Hg, dithiobishomoantipyrine or bis- [1-phenyl-2-ethyl-3-methylpyrazolone, 4,4'-disulfide (A)] was found to take up 1 atom of Hg smoothly. As the work has thus far appeared only in difficultly accessible publications (v. Miskolczy, *Diss. Budapest* 1909; *Ann. 7th Internat. Congr. Appl. Chem. (London)*, 1909, Sect. Org. Chem.), it is again briefly described in the present paper. Two mols. homoantipyrine in enough alc.-free CHCl₃ so there is no crystn. on cooling below 0° are treated with 1 mol. S₂Cl₂ in 10 parts CCl₄ at such a rate that the temp. does not rise above 5°; the resulting thick magma is filtered with suction, washed with CCl₄ at once spread on clay, finally dried *in vacuo* over paraffin, dissolved in luke-warm dil. HCl, filtered through a hot-H₂O funnel and the HCl salt which at once seps. in fine needles is drained off and digested with cold H₂O; it dissociates spontaneously into HCl and the free A, vivid yellow crystals from C₆H₆, m. 199-200°, mol. wt. in boiling alc. 482 (yield, 4.5-5.0 g. from 10 g. homoantipyrine). When it is shaken in CHCl₃ with excess of Hg, it momentarily turns green and in about 10 min. the reaction is complete; the traces of HgS are filtered off, the excess of CHCl₃ removed and 2-3 vols. abs. alc. added, whereupon the compound C₂₄H₃₀O₂N₂S₂Hg seps. in faintly yellowish green prisms, m. 230-1° (decompn.), at once become black when moistened with (NH₄)₂S. In view of the fact that these antipyrine disulfides have the calcd. mol. wts. in boiling alc. but add Hg smoothly and quant. in cold CHCl₃, v. K. concludes that a dissociation into radicals in these and similar cases occurs under the influence of the chem. affinity of Hg for S only at the first moment of the action of the Hg and the nascent radicals at once reunite through the Hg bridge to form stable mercaptides. C. A. ROUILLER

Dicyanodimethyl sulfide. WILHELM STEINKOFF. *Ber.* 53B, 1671(1920).—The S(CH₃CN)₂ recently described (*C. A.* 14, 3419) had already been prepd. in a similar manner by v. Zweigbergk (*C. A.* 7, 1000). CHAS. A. ROUILLER

Phenyl-*o*-tolyltellurium compounds. KARL LEDERER. *Prag. Ber.* 53B, 1674-80(1920); cf. *C. A.* 14, 3234; 15, 79; and earlier papers.—With Grignard reagents diaryltellururionium dihalides yield triaryltellururionium salts which are reduced by an excess of the Grignard reagent to tellurides. This reduction may occur in 3 ways: (1) R₂TeR'X + R'MgX = R₂Te + R' + MgX₂; (2) R₂TeR'X + R'MgX = RTER' + RR' + MgX₂; (3) a combination of (1) and (2). The present paper deals with a case of the last type. To the Grignard soln. from 193.65 g. *o*-BrC₆H₄Me and 28.3 g. Mg is slowly added 100 g. Ph₂TeBr₂, the mixt. boiled 0.5 hr., decompd. with concd. NH₄Cl, the Et₂O, PhMe and unchanged BrC₆H₄Me distd. off under atm. pressure in CO₂ and the residue fractionated under 18 mm. The portion b₁, 181-210° is treated in 0.5 l. cold Et₂O with Br. Ph₂TeBr₂, m. 203-4° after crystn. from CHCl₃ or CS₂, seps. first, while the Et₂O mother liquors yield 20.5 g. crude phenyl-*o*-tolyltellururionium dibromide (A); a further 5-6 g. is obtained by evapg. the Et₂O mother liquors to dryness, repeatedly extg. the red-brown resin that remains with boiling H₂O, pptg. the MeC₆H₄-TePh from the aq. ext. with NaHSO₄, taking it up in Et₂O and treating with Br. Sim-

ilarly, from 100 g. (*o*-MeC₆H₄)₂TeBr₂ with PhMgBr is obtained a mixt. of dibromides sepd. by fractional crystn. from CHCl₃-EtOH and yielding 19 g. A. A softens 150-1°, m. 154-5°, seps. from alc. in broad needles which under the microscope show the form of elongated 8-sided tablets, also of 4-sided columns, from PhMe only in the column form; 20 g. slowly added to the Grignard soln. from 20 g. MeI and 3.51 g. Mg and boiled 0.5 hr. yields somewhat more than 10 g. *phenyl-o-tolyl telluride*, faintly orange-yellow oil, b₂₀ 212-3°; with dry HCl in Et₂O this gives the *dichloride*, 4-sided columns and 6-sided tablets from PhMe, softens 178°, m. 179-80°; *diiodide*, from the telluride and I in Et₂O, garnet-red 4-sided microcolumns from PhMe, 6-sided tablets from alc., softens about 169°, m. 172-3°. *Oxide*, from the dibromide heated 0.5 hr. on the H₂O bath with NH₄OH, granules of microprisms from xylene, softens 214°, m. 216-7°. *Mercuric iodide compound*, Ph(MeC₆H₄)₂Te.HgI₂, from equimol. amts. of the components in boiling alc., yellow 4-sided microcolumns and step-like crystals, softens about 123°, m. 133-4°, apparently seps. with alc. of crystn. *Methylphenyl-o-tolyltelluronium iodide*, from 1 g. PhTeC₆H₄Me allowed to stand 8 days in 10 cc. MeI, needles, softens 118-7°, m. 119-20°, decomp. into its components.

CHAS. A. ROULLER

Tetraethylammonium (preliminary communication). HANS HEINRICH SCHLUBACH. Bayr. Akad. Wiss. München. Ber. 53B, 1689-93(1920).—NEt₄Cl (0.5 g.), dry and free from alkalis, was electrolyzed in liquid NH₃ (distd. from Na) at -78° with a 0.1-amp. current in an app. in which moisture and atm. O can be completely excluded (the app. will be described in detail later); a clay cell was used as diaphragm. At the instant the circuit is closed there at once appear at the Pt cathode dark blue streaks ("Schlieren"), which in a few min. spread out over the whole cathode chamber and form a deep blue soln. the intensity of whose color increases as the electrolysis proceeds. If, after about 1.5 times the calcd. amt. of current has been used, the deep blue-black soln. is allowed to stand at -78° the color persists for some hrs. and then slowly fades out. The soln. shows strong absorption not only in the violet but also in the red. When the freshly prepd. soln. is evapd. under 15 mm. it is slowly decolorized, although the temp. sinks below -100°, and after complete evapn. of the NH₃ there remains only a little unchanged NEt₄Cl; if the evapn. is carried out under atm. pressure (-33°), the decolorization is markedly more rapid and there remains, besides unchanged NEt₄Cl, some NEt₃. If the soln. is poured upon somewhat less than the calcd. amt. of I, there is immediate decolorization, and evapn. of the NH₃ and recrystn. of the residue from H₂O gives 80% NEt₄I. If, during the electrolysis, dry O is introduced at the cathode the streaks are at once decolorized and on evapn. there remains a faintly yellowish residue which, by analogy with K, might be expected to be a peroxide but 0.2747 g. treated with H₂O evolves only 1.9 cc. gas, and titration of the soln. with H₂SO₄ and AgNO₃ reveals the presence of 8% unchanged NEt₄Cl and 70% NEt₄OH. When KI is electrolyzed in the same app. and dry C₂H₂ is introduced at the cathode during the hydrolysis, HC:CK is formed. If C₂H₂ is similarly introduced during the electrolysis of NEt₄Cl decolorization occurs but treatment of the product with H₂O shows that no product analogous to the C₂HK is formed. Except for this last reaction, the free NEt₃ behaves exactly like K and Na, the only difference being that its decompn. sets in at low temps. while in the case of the alkalis it has not been possible as yet to effect their decompn. with even the most powerful electrical forces. In preliminary expts. it was found that NMe₄I and NPr₄I show the same phenomena on electrolysis as NEt₄Cl but that NEt₄PhI does not, PhNEt₃ at once sepg. at the cathode. C. A. R.

Tannins. VI. KARL FREUDENBERG. Chebulinic acid. II. BRUNO FICK. Univ. Kiel. Ber. 53B, 1728-36(1920); cf. C. A. 14, 180.—Further details are given as to the properties of the cryst. tannin (A) and the amorphous acid (B) which result from the cleavage by H₂O of chebulinic acid (C). That A is a digalloylglucose has been confirmed by fermentative degradation, elementary analyses and mol. wt. detns. in

boiling Me_2CO . It is not attacked by emulsin, phaseolunatae nor yeast ext. and therefore probably neither of the 2 gallic acid residues stands in the same relation to the sugar as the gallic acid in 1-galloyl- β -glucose (Fischer and Bergmann, *C. A.* 13, 1466). Possibly A is a deriv. of α -glucose but it is more probable that the 1-position of the sugar is unoccupied; presumably the B is attached at this point. The study of B has not been completed. It does not cryst. in the free state; the compn. of the cryst. Tl and brucine salts indicates that it is a dibasic acid $\text{C}_{14}\text{H}_{14}\text{O}_{11}$; possibly it contains a 3rd, more weakly acid group, for titration with litmus gives an equiv. wt. of approx. $1/3\text{C}_{14}\text{H}_{14}\text{O}_{11}$. Assuming this compn. for B, C can be considered as being derived from 1 mol. each of A and B by the loss of $2\text{H}_2\text{O}$, giving for C the compn. $\text{C}_{14}\text{H}_{12}\text{O}_{10}$, which would require 50.67% C and 3.75%; the average of reliable detns. in the literature is 50.60, and 3.65, resp. Mol. wt. detns. by titration and by the b. p. method in Me_2CO give values agreeing with that calcd. for the above formula. The possibility is not excluded entirely that B may have 0.5 the above mol. wt. (say $\text{C}_7\text{H}_6\text{O}_4$) or that it may be a mixt. of $\text{C}_7\text{H}_6\text{O}_4$ and $\text{C}_7\text{H}_8\text{O}_4$, or finally there may be in C a third mol. of gallic acid which is easily split off. C (200 g., anhydrous) is boiled under a reflux in 8 l. of H_2O for 22 hrs., then concd. in the course of 4 hrs. to 500 cc., freed from most of the gallic acid with Et_2O , evapd. to 0.5 its vol., freed from the rest of the gallic acid until it no longer gives the KCN reaction, allowed to stand 8 days at 0° , filtered from the A that seps., made up to 300 cc., treated with 828 cc. of 0.5 N TiHCO_3 so that the soln. is still faintly acid to litmus, filtered from the brown granular ppt. (D), allowed to stand 2 days on ice, again filtered, concd. *in vacuo* to 400 cc., shaken out 6 times with 75-cc. portions of neutral AcOEt to remove the last traces of A, freed from the AcOEt remaining in the liquid layer with Et_2O (freshly decanted from Na) and from the Et_2O *in vacuo* and after 24 hrs. the cryst. Tl salt is filtered off. There are thus obtained, in g. (the figures in parentheses give the mols., assuming that the formulas given above for B and C are correct) from 200 g. C: A 67 (0.56); gallic acid 35 (0.83); B 31 (0.35). The 67 g. A contain 47 g. gallic acid (1.11) and 25 g. glucose (0.56). There thus remain unaccounted for 0.06 mol. gallic acid, 0.44 mol. glucose and 0.65 mol. B. The missing glucose may have remained, partly free and partly as a non-crystallizable monogalloylglucose, with the rest of the gallic acid in the mother liquors of the cryst. Tl salt but it is more probable that it is present with the main portion of B (0.65 mol.) in the amorphous Tl ppt. (D). C loses no CO_2 in H_2O at 100° and no cryst. salt, as described by Richter (*Arch. d. Pharm. Inst. Berlin* 9, 85(1912)), could be obtained. Its mol. wt. in aq. Me_2CO as detd. by titration with litmus (allowing 1.5–1.7 cc. 0.1 N alkali per g. for the phenolic HO groups) is about 800; by the b. p. method in Me_2CO , 761–815. A, purified by nearly neutralizing the crude product in H_2O with TiHCO_3 , filtering, evapg. *in vacuo* to a thin sirup, exhausting with neutral AcOEt , evapg. *in vacuo* and crystg. from H_2O , seps. in needles with 15.32% H_2O ; mol. wt. (anhydrous) in boiling Me_2CO 460–60. It dissolves in NH_4OH with red color at once changing to yellow and reappearing on shaking, and gives a very faint KCN reaction, probably due to gallic acid split off. On degradation with tannase, as previously described for hamameli tannin (*C. A.* 14, 3413), 1 g. A after 6 days requires 42.6 cc. 0.1 N alkali for its neutralization (calcd., 41.1 cc. + 1.5 cc. for the phenol HO groups), and after removal of most of the gallic acid addition of fresh tannase produces no further increase in acidity. The glucose found (mean of gravimetric, titrimetric and polarimetric detns.) was 34.4%; calcd. 36.2. As in the case of hamameli tannin there remains a small amt. of a tannin-like residue (also formed when a mixt. of 2 mols. gallic acid and 1 mol. glucose is treated with tannase), the formation of which was previously ascribed to traces of an admixed oxidase but which is now believed to be due simply to the action of the atm. O; it amts. at most to 0.5% of the mixt. of gallic acid and glucose. Di[triacetylgalloyl]triacytylglucose, from A in $\text{C}_2\text{H}_5\text{N}$ with Ac_2O , needles from alc., m. $177-9^\circ$, $[\alpha]_D$ 40.7° (Me_2CO). B, prepd. from the Tl salt

by treating with HCl, finally in aq. Me_2CO , until the liquid contains neither Tl nor Cl, filtering from the TlCl and evap. *in vacuo*, is a sirup; 8 g. in 10–20 cc. H_2O added to 16 g. brucine in 100–50 cc. warm alc. yields 18 g. of the brucine salt, $\text{C}_{44}\text{H}_{41}\text{O}_{11}(\text{C}_{27}\text{H}_{29}\text{O}_4\text{N}_3)_2$, spears from H_2O , darkens 200° , m. about 50° higher (decompn.). The Tl salt, spears from H_2O , is obtained by decomp. the brucine salt in warm aq. MeOH with very dil. aq. $\text{Pb}(\text{OAc})_2$, decomp. the thoroughly washed Pb salt, suspended in much H_2O , with H_2S , removing the H_2S *in vacuo*, again pptg. with $\text{Pb}(\text{OAc})_2$, washing the ppt. with H_2O and 96% alc. until entirely free of brucine (HNO_3 test), decomp. with H_2S evap. *in vacuo* to a sirup and almost neutralizing in H_2O with THCO_2 . Attempts to acetylate, methylate and carbomethoxylate B have thus far been without result. When B is heated to $320\text{--}40^\circ$ under 12 mm., however, it gives a little pyrogallol. C. A. R.

Action of mercaptans and hydrogen sulfide on *o*-chloromercuribenzoil chloride. GEORGE SACHS. Univ. Wien. Ber. 53B, 1737–45(1920).—Mercaptans act on *o*- $\text{ClHgC}_6\text{H}_4\text{COCl}$ (A) according to the equation $\text{A} + \text{RSH} = \text{ClHgC}_6\text{H}_4\text{COSR} + \text{HCl}$, while H_2S reacts according to the equation $2\text{A} + \text{H}_2\text{S} = \text{S}(\text{HgC}_6\text{H}_4\text{COCl})_2(\text{B}) + 2\text{HCl}$. *o*- $\text{ClHgC}_6\text{H}_4\text{CO}_2\text{H}$ (C) and PhHgCl do not react with EtSH at room temp. nor on the H_2O bath, but $\text{ClHgC}_6\text{H}_4\text{CO}_2\text{Na}$ reacts quite rapidly at room temp. according to the equation $\text{ClHgC}_6\text{H}_4\text{CO}_2\text{Na} + \text{EtSH} = \text{EtSHgC}_6\text{H}_4\text{CO}_2\text{H} + \text{NaCl}$; *i. e.*, the reaction takes place when the HCl formed is simultaneously neutralized. Only at 150° in sealed tubes does EtSH react with C and PhHgCl , and then according to the equation $\text{C} + \text{EtSH} = \text{BzOH} + \text{ClHgSEt}$. Similarly B with boiling MeOH gives $\text{ClHgC}_6\text{H}_4\text{CO}_2\text{Me} + \text{BzOMe} + \text{HgS} + \text{HCl}$. *o*-Sulfidomercuribenzoil chloride (B), obtained in 2.3 g. yield from 3.5 g. A in Et_2O treated 4 hrs. with H_2S dried with P_2O_5 and satd. with Et_2O vapor, and allowed to stand overnight, is a faintly yellowish ppt., does not m. 280° , evolves H_2S with concd. HCl and is entirely insol.; when it is shaken or boiled with an aq. suspension of HgO the latter is not converted into HgS , indicating that the S in B is really attached to the Hg; this is further confirmed by the action with boiling MeOH, 1.3 g. B with 20 parts MeOH giving BzOMe, 0.4 g. HgS and 0.3 g. *o*- $\text{ClHgC}_6\text{H}_4\text{CO}_2\text{Me}$, m. $181.5\text{--}2.0^\circ$; after standing 1 yr. it m. $149\text{--}9.5^\circ$ even after recrystn.; Schrauth, Schoeller and Hueter give $142\text{--}62^\circ$ (C. A. 14, 3086). The $181.5\text{--}2.0^\circ$ product, sapond. with alc. KOH, dild. with H_2O , pptd. with AcOH, dissolved in a few drops of concd. $(\text{NH}_4)_2\text{CO}_3$ and seeded, gives *o*- $\text{HOHgC}_6\text{H}_4\text{CO}_2\text{NH}_4$; the sapon. product was, therefore, $\text{HgC}_6\text{H}_4\text{CO}_2\text{O}$.

Ethyl *o*-chloromercuriethiolbenzoate (0.7 g. from 1.5 g. A in boiling C_6H_6 with 0.3 g. EtSH in C_6H_6), faintly yellow microleaflets from Et_2O , m. $142.5\text{--}4.5^\circ$, evolve, no HCl with MeOH. C (1 g.) in Me_2CO heated 8 hrs. at 150° with 0.3 g. EtSH gives 0.6 g. of silvery scales having the compn. of ethylmercaptomercuric chloride; some BzOH was isolated from the mother liquors. Similarly 0.75 g. PhHgCl in a sealed tube with EtSH in Me_2CO gives 0.4 g. EtSHgCl. From 3 g. $\text{ClHgC}_6\text{H}_4\text{CO}_2\text{Na}$ in 75 cc. Me_2CO allowed to stand 1 day with 1 g. EtSH, then boiled 1 hr. and filtered hot is obtained 2.2 g. *o*-mercaptomercuribenzoic acid, crystals from Me_2CO , m. partially $138.5\text{--}40^\circ$, at the same time forming HgS , sol. in soda, evolving a distinct mercaptan odor when boiled in this soln. or in H_2O suspension. $\text{HgC}_6\text{H}_4\text{CO}_2\text{O}$ (5 g.) reacts instantly with 15 g. SOCl_2 ;

on boiling a part dissolves but seps. again on cooling. Filtered, washed with CHCl_3 and freed from an amorphous impurity by 2 crystns. from C_6H_6 it gives 3.5 g. pure A, m. 173.5° . From 1.6 g. C, m. $222\text{--}38^\circ$ (decompn.), boiled 1 hr. with 10 g. SOCl_2 are obtained, besides 1.5 g. unchanged C, only decompn. products already giving the Hg reactions. *o*- $\text{HSHgC}_6\text{H}_4\text{CO}_2\text{H}$ with SOCl_2 likewise gives only C and possibly some HSHgCl .

CHAS. A. ROULLER

Molecular coefficient of refraction, its additive behavior and its applicability for the determination of constitution. I. FRITZ EISENLOER AND EDGAR WÖHLISCHE.

Univ. Königsberg (Pr.). *Ber.* 53B, 1746-66(1920).—It was shown some time ago that for a liquid org. compd. the product of the index of refraction into the mol. wt. gives within certain limits an expression which like those for mol. refraction and dispersion furnishes a numerical relationship between mols. and their atoms and the way in which they are united (*Spectrochemie organischer Verbindungen*, 1912, p. 12), and the hope was expressed that the method of the "mol. coeff. of refraction," as the term $M \times n_D^{20}$ was designated, might prove to be a valuable addition to the mol. refraction and dispersion methods, as in the latter, in the expression $[(n^2 - 1)/(n^2 + 2)](M/d)$ involving the index of refraction and the sp. gravity, only relatively few constitutional influences manifest themselves. The present paper is a summary of the results obtained in the study of the new method, which has fully come up to expectations; a full account will be published elsewhere. On the basis of measurements taken from the literature on about 400 compds. carefully considered as to purity, E. and W. find for their new method that the additive relationship between mols. on the one hand and residues and manner of union on the other is so general that it is not limited to chemically closely related substances and that it can under certain conditions be applied to the detn. of the purity of compds.; constitutional influences manifest themselves distinctly and can be expressed according to numerical laws; these influences manifest themselves more markedly than in the mol. refraction and dispersion methods. The basic value for the group CH_3 was deduced from compds. only of the normal series (15 paraffins, 15 primary alcs., 7 aldehydes, 12 ketones, 9 acids and 27 esters) (cf. *C. A.* 5, 1218); using this basic value, the normal paraffins give the equiv. for H_2 and for singly bound C. The following values are obtained (the numbers in parentheses give the probable errors): CH_3 20.56 (0.010), C 25.55 (0.033), H_2 -4.99 (0.033), O' in alcs. 26.54 (0.032), O' in ethers 22.97 (0.043), O' in aldehydes 17.40 (0.058), O' in ketones 16.98 (0.058), double bond $\text{C}=\text{C}$ -6.17 (0.063). The max. error in $M \times n_D^{20}$ may be taken as 0.2; with pure material all deviations beyond this may be ascribed to constitutional influences. In acyclic compds. the introduction of a side chain on the 2-C atom lowers $M \times n$ by 0.2 while side chains on C atoms further removed from the end one raise $M \times n$ by 0.45; a combination of the two gives an average value differing but little from that for the normal chain. The influence of the ring in cyclic, non-aromatic compds. is not easily detd. because the not very numerous detns. on the parent substances of the hydrocarbons, alcs. and ketones are in part divergent and on the other hand in homologous compds. the influence both of the ring and of substitution manifests itself. Until further data are available the following values may be taken as representing the influence of the ring: 3-membered (3-R) -5.5, 4-R -4.9, 5-R -4.2, 6-R -3.3, 7-R -2.2, 8-R -1.1. Introduction of 1 side chain into the ring produces a further depression of -0.75; in disubstituted derivs. the depression is in general greater than in monosubstituted derivs. and increases in the order o, m, p. Two side chains on one C atom of the ring produce but an insignificant change in the depression, except that when a *gem*- Me_2 group enters a ring in the *p*-position to a substituent already present it changes the value to one approaching that for the mother substance. An ethylene union in polymethylenes has no influence on the ring decrement in the mother substances, but in the homologs while monosubstitution at the doubly bound C leaves the normal value unchanged, as the side chain and the double bond become further removed from each other there is a renewed depression; in the case of disubstituted derivs. these relations are even more pronounced, substitution at both the unsatd. C atoms actually producing a positive increment which changes to increased depressions as the substituents are removed away from the double bond. The semicyclic behave just like the endocyclic compds. in this respect. The value for the aromatic nucleus is -21.20; increasing number of side chains produces increasing positive increments which are greatest with the least sym. forms; the difference between the increments of the least sym. and the

sym. forms is $0.5 \times$ the number of substituents and the increment for the *p*-comps. is to that for the *m*-derivs. as 0.7:1. Aliphatic acids give values lower by -2.48 than those calcd. (using the const. for ketonic O in the calcn.); for HCO_2H this depression is only -0.97 . This anomaly in aliphatic acids (and esters) is possibly due to the fact that they form loose rings, $\text{RC}=\text{O}$, the influence of which is more pronounced when

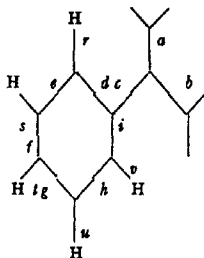


the ring is substituted ($\text{R} = \text{substituent}$) than when it is not, as in formic acid and esters ($\text{R} = \text{H}$).

CHAS. A. ROULLER

The principle of the constant sum of energies of formation and their distribution on the unions in aromatic substances. A. L. v. STREIGER. Bayr. Akad. Wiss. München. Ber. 53B, 1766-72 (1920); cf. C. A. 14, 3232.—In the earlier paper it was shown that the aromatic ring C atoms have the same distribution of valence as the C atoms in graphite and on the assumption of the energetic equivalence of all C-C and C-H unions in vaporized aromatic hydrocarbons consisting only of 6- or condensed 6-membered rings there were deduced relationships between the heats of combustion of these hydrocarbons which agreed with the greatest exactitude with Stohmann's exptl. data. It was pointed out that these results are insofar surprising as the study of substitution in aromatic chemistry points to marked differences in the valence and union relationships of different positions of aromatic hydrocarbons. The two sets of phenomena can be explained only if there are relationships between the energies of formation of the individual unions which mutually compensate the differences in energy values of the C-C and C-H unions, assumed in the calcn. of the heats of combustion to be equal. In the present paper is formulated a principle of the distribution of energies of formation of atomic unions in gaseous aromatic hydrocarbons. Let the accompanying figure represent a section through any aromatic 6-membered ring system and consider an aromatic C atom with three satd. main valences and a fourth valence which can be satd. only intermol., i. e., a "free" valence of a lower order of magnitude, as being, energetically, purely tervalent. Assume also the most general case that all the C-C and C-H unions are different and represented by the letters *a*, *b*, etc. Then, in spite of their being different, the exptl. heats of combustion can be summated by the const. values *x* and *y* for the C-H and C-C unions if, e. g., the following relationships exist between the actual energies of formation and *x* and *y*: $a/2 + b/2 + c/2 = c/2 + d/2 + i/2 = 3/2y$; $d/2 + e/2 + f/2 + g/2 + h/2 + i/2 + j/2 + k/2 + l/2 + m/2 + n/2 + o/2 + p/2 + q/2 + r/2 + s/2 + t/2 + u/2 + v/2 + w/2 + x/2 + y/2 = 3/2y$. On dissociation of a gaseous ring hydrocarbon mol. into its gaseous atoms, then, for each =CH group combined with 2 aromatic ring C atoms and for each aromatic C atom combined with 3 aromatic ring C atoms there must be expended a const. quantum of heat of dissociation, $k_1 = y + x$ and $k_2 = 3/2y$, although in each individual case it is made up of different components. *y* may, therefore, be defined as the mean value of the heat of formation of three C-C unions between an aromatic ring C atom with 3 other aromatic ring C atoms, while *x* is merely equal to $k_1 - y$; nevertheless *x* gives an expression of the proper order of magnitude for the energy value of the C-H union, as the actual values of the aromatic C-C unions, even if they do vary, are all of the same order of magnitude. Suppose, now, that the union *c* in the figure is strengthened, say by some substitution in a part of the mol. not shown in the figure. Then *d* + *i* must decrease by an amt. equal to the increase in *c*; the change in *d* and *i* will likewise produce a change in all the other C-C and C-H unions in the ring. This principle formulated for gaseous aromatic hydrocarbons is confirmed by the work of Fajans (C. A. 14, 1623) who found that the total energy of formation of the C-C unions per g. atom of C is the same, within 2%, in the diamond, graphite and amorphous C. Analogous considerations can be applied to energetically quadrivalent C in its compds. with H, i. e., to the aliphatic hydrocarbons. Of special interest in this connection is the fact that the heat

of combustion of the $=CH_2$ is always almost the same (154–8 k. cal.), whether detd. from the difference in the heats of combustion of homologs of the satd. aliphatic, olefin, acetylene or benzene series.



CHAS. A. ROUILLER

The isomeric forms of mesityl oxide-oxalic acid and its esters. W. DIECKMANN. Akad. Wiss. München. Ber. 53B, 1772–82(1920).—The two isomeric acids (and their esters) have always been considered typical keto-enol isomers, the α -form (A) being assigned the enolic structure $Me_3C:CHCOCH:C(OH)CO_2R$. That A has this structure is beyond doubt, but the view that the β -form (B) is the corresponding ketone is shown to be untenable. In keto-enol isomers of the type $RCOCH_2COR'(C) \rightleftharpoons RCOCH:C(OH)R'$, the Claisen rule that the tendency to enolization, and hence the enol content at equil., increases with the acidity of the acyl groups has been fully confirmed. In oxalyl derivs. of satd. ketones of the general structure $RCOCH_2COCO_2R$, the enol content at equil. is about 90% and on distn. the enol forms remain. On the other hand, with A and B at equil. there is only a few % of A and on distn. A changes for the most part into B. The same difference in behavior is shown just as strikingly by the free acids; in the case of the satd. compds. the enols are not changed by recrystn. from boiling H_2O while A ($R = H$) is changed almost completely into B. Again, in compds. of the type C the rearrangement velocity in alc. is so great, even in the absence of all catalysts, that equil. is almost reached within 1 day at 25° ; alkalies, even in minimal concn. (0.0001 N), accelerate the rearrangement enormously (equil. is reached in a few min.), while acids produce but a slight acceleration (hardly perceptible with 0.002 N acid, 2–3 fold with 0.01 N, increasing with higher concns. about proportionately to the acid content). With A, on the other hand, the rearrangement in alc. into B is so slow that at room temp. equil. is reached only after months; alkalies, even up to 0.002 N, do not accelerate the reaction nearly so much as in the case of C, while acids produce a marked acceleration (100-fold with 0.002 N acid, 200-fold with 0.01 N; higher concns. produce no marked effect). In view of these facts, D. believes that A and B are not keto-enol isomers but that B is a cyclic isomer of A, viz., α,α -dimethyl- α,β -dihydro- γ -pyrone- α' -carboxylic acid (D), $O.CMe_2CH_2CO.CH:CCO_2R$. Such a structure for

B agrees better with all its properties (chem. and physical) than the keto structure corresponding to A. Claisen himself, who first prepd. A and B, originally held the same view as to their structure (Ber. 24, 115(1891); Kerstien, Diss. München 1890)). On titration with Br in alc. the Me ester of A absorbs somewhat more than the calcd. amt. of Br; the amt. absorbed, moreover, depends greatly on the exptl. conditions (cf. Scheiber and Herold, C. A. 8, 3426) and D. believes that the excess of Br used up is not due to the presence of a dienol but that the Br addition product first formed splits off a little HBr with a velocity depending upon the nature of the solvent and that the resulting

Br-substitution product then also takes up Br. This phenomenon is even more marked in the case of hydroresorcinols, which on titration in MeOH at -15° absorb approx. 2 mols. Br; again, while acetylacetone in equil. in C_6H_5N , when satd. with AcOH and titrated in alc. with Br, takes up about 2 mols. (Meyer, C. A. 7, 993), if the C_6H_5N soln. is slowly added to alc. Br containing an excess of HCl, only about 1 mol. Br is absorbed. On account of these complications the titration of A with Br is not very sharp but by keeping the conditions exactly alike the enol content can be detd. with sufficient accuracy to permit of following the course of the rearrangement. The Me ester of A required 1.1, 1.2, 1.4 and 1.8 mols. Br in MeOH at -15° , abs. EtOH at -15° , 96% alc. at -15° and 96% alc. at 0° , resp. The rearrangement velocity in an approx. 1% soln. in abs. alc. gives a slowly rising velocity const. $K = 0.4343 (K_1 + k_2)$ of 0.000005-0.00001; at equil. there is about 3% A. The rearrangement velocity is about the same in MeOH and also in 90% alc. Et propionylpyruvate, b_{11} 128-9°, absorbed 1.2 and 1.6 mols. Br in MeOH at -10° and 96% alc. at 0° , resp.; according to the Br titration it contains 80-90% mol. The 1% soln. in abs. alc. has a similarly high enol content which does not change markedly after several days in the presence of 0.1 N HCl. The free acid (from the ester with concd. HCl) is shown, by the Br titration, to be the enol form after crystn. from boiling H_2O . Benzoylpyruvic acid and its Et ester behave similarly. A (Me ester) with 1-2 mols. $PhNHNH_2$ in concd. AcOH, either on short standing or long warming on the H_2O bath, gives methyl 1-phenyl-5-[β -dimethylethenyl]pyrazole-5-carboxylic acid, crystals from MeOH, m. 108° ; free acid, needles from 50% AcOH, m. 167° . The β -ester (D), on the other hand, with $PhNHNH_2$ gives the corresponding phenylhydrazone of D, intensely yellow crystals from MeOH, m. 163° ; the free acid (D) likewise yields a yellow phenylhydrazone. C. A. R.

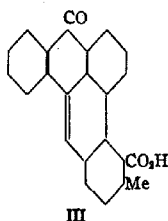
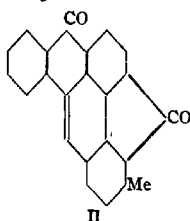
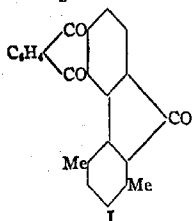
Geometric isomerism of polymethylenes. A. SKITA. Univ. Freiburg i. Br. Ber. 53B, 1792-806 (1920).—Thus far there were available no general chem. methods for prep. the different stereoisomers of hexamethylene and especially for obtaining at will from the starting material the theoretically possible configurations. The results of the present work seem to indicate that in the hydrogenation of double bonds in acid soln. (e. g., catalytically with Pt) the production of *cis*-forms is favored while in alk. and neutral mediums the *trans*-forms are more readily produced. 2,4,5-Me₃C₆H₃OH (50 g.) in 120 cc. AcOH, 40 cc. colloidal Pt soln. (0.5% Pt), 25 cc. of 10% H₂PtCl₆, 40 cc. of 10% aq. gum arabic and 20 cc. H₂O shaken at room temp. with H under an excess pressure of 1-3 atm. absorbs about 4 instead of the calcd. 3 mols. of H in 2 hrs. and gives, besides the desired alc. (see B, below), 45% of the hydrocarbon (A, below); by interrupting the reduction when 3 mols. of H have been absorbed, a 75% yield of B and 20% of A are obtained. The reaction mixt. is made alk. with soda, distd. with steam and the distillate fractionated *in vacuo*. *cis*-1,2,4-Trimethylcyclohexane (A), b_{11} 33° , b. $144.8-5.8^{\circ}$, does not decolorize Br. *cis*-1-Hydroxy-*cis*-2,4,5-trimethylcyclohexane (B), b_{17} 84° , b. $191-3^{\circ}$; phenylurethan, crystals from alc., m. 83.5° . B (68 g.) in 120 cc. AcOH treated below 70° with 280 cc. of Beckmann's CrO₃ soln. containing the calcd. amt. of available O, heated 1 hr. at 80° , made alk., distd. with steam, shaken with concd. NaHSO₄, filtered, decompd. with soda and again distd. with steam gave 60 g. *cis*-2,4,5-trimethylcyclohexanone (C), b. 193° ; semicarbazone, needles from alc., m. 204° (yield, quant.); oxime, crystals from alc., m. 105° (yield, 76%). C with Pt and H under 1-2 atm. excess pressure absorbs the calcd. amt. of H in 10 min., giving B. A, B and C have higher sp. gravities and indices of refraction and smaller mol. refractions than the corresponding compds. obtained by the Sabatier method with Ni as the catalyst (v. Auwers, C. A. 14, 2160), indicating that the former are the *cis*-, the latter the *trans*-compds. With 8 times the calcd. amt. of Na in aq. Et₂O, however, C gives *trans*-1-hydroxy-*cis*-2,4,5-trimethylcyclohexane (D), b_{11} 112° , b. 196° ; phenylurethan, m. 95° ; hydrogen phenalate, crystals from Et₂O-ligroin, m. $81-3.5^{\circ}$. D with Beckmann's acid gives C, showing

that B and D are really *cis-trans* isomers with respect to the HO group, and comparison of their optical consts. shows that D is the *trans*-form. D, however, is not identical with the alc. obtained by the Sabatier method; therefore, the isomerism of the alcs. prepd. by the Pt and Ni methods does not depend on different positions of the HO but of the Me groups, and the alc. obtained by the Ni method is probably the *trans*-2,4,5-trimethyl compd. 2,4,5-Me₃C₆H₃NH₂ with Pt and H at 60° absorbs the calcd. amt. of H in 2 hrs., giving *cis*-1-amino-*cis*-2,4,5-trimethylcyclohexane (E), b_p 74°, b. 188–90° (yield, 85%); *picrate*, sinters 208°, m. 212°; *hydrochloride*, hygroscopic but not deliquescent crystals from EtOH-Et₂O, m. 227–8°; *d-α*-bromocamphor-*π*-sulfonate, needles from alc., m. 171.5°; *acetyl derivative*, needles from AcOEt, m. 100°; *benzoyl derivative*, m. 107.5–8.0°; *phenylthiourea*, needles from alc., m. 164°; *phenylurea*, oil. E is also obtained from the oxime of C in boiling alc. with Na-Hg and AcOH or with H and Pt in AcOH-HCl but with Na and alc. (At this point—p. 1895 of the exptl. part—a paragraph has evidently been left out by mistake.—ABTRACTOR) the oxime yields the *trans*-amino isomer (F) of E, b. 187–8°; *picrate*, m. 187.5°; *hydrochloride*, crystals from H₂O or EtOH-Et₂O, carbonizes 260°; *d-α*-bromocamphor-*π*-sulfonate, crystals from C₆H₅-Et₂O-ligroin or better from 1,2,4-trimethylcyclohexane, decomps. 205°; *benzoyl derivative*, needles from dil. alc. or 50% AcOH, m. 174.5°; *phenylurea*, needles from Et₂O, m. 169°; *phenylthiourea*, crystals from alc. or Et₂O, m. 155°. That E and F are the *cis*- and *trans*-forms, resp., is indicated both by chem. analogy with the lactam-forming and non-lactam-forming NH₂ esters (C. A. 2, 274) and by their physical consts. With HNO₃ E gives B while F yields D. In the prepn. of E, the mother liquors from the *picrate* yield a small amt. (5%) of another *picrate*, m. 153°, the free base of which, b. 181–2°, is isomeric with E and F; *thiourea*, m. 110°. Although its physical consts. agree within the limits of exptl. error with those of E, the base is undoubtedly different from E and is probably a *cis*-1-amino-*cis-trans*-2,4,5-trimethyl form. The following values for d_4^{20} , n_D^{20} and $E_{2\%}^{1\text{cm}}$, resp., were detd. by A. v. Auwers: B 0.912, 1.463, –0.11; isomer prepd. by the Sabatier method 0.898, 1.458, 0.07; C 0.905, 1.450, 0.02; S. isomer 0.896, 1.448, 0.23; A 0.790, 1.434, 0.04; S. isomer 0.778, 1.429, 0.21; E 0.864, 1.462, –0.13; F 0.857, 1.458, –0.09; B 0.906, 1.461, –0.03.

CHAS. A. ROUILLER

Synthesis of a phenanthroanthraquinonefluorenone. ALFRED SCHAARSCHMIDT AND JOHANN HERZENBERG. Techn. Hochschule Berlin. Ber. 53B, 1807–14 (1920); cf. C. A. 13, 601.—1,2-C₆H₄(CO)₂C₆H₃(NH₂)Me diazotized in concd. H₂SO₄ gives by the Sandmeyer method in the cold 90% of the 1-Cl compd., m. 170–1°; this is chlorinated about 8 hrs. at 200° until it gains 33% in wt., then heated 3 hrs. at 125° with 20 parts concd. H₂SO₄ and a little H₂BO₃ and the crude aldehyde is washed with soda, purified through the NaHSO₃ compd. and oxidized with CrO₃ in 7 parts AcOH (10 g. CrO₃ for 7 g. aldehyde), giving 85% of 1,2-C₆H₄(CO)₂C₆H₃ClCO₂H, which, converted into the chloride with PCl₅ and condensed with *p*-xylene in the presence of AlCl₃, yields quant. 1-chloro-2-*p*-xyloylantraquinone, bright yellow needles from AcOH, m. 175–6°; 13 g. of this heated 6–7 hrs. at 180–90° with 100 cc. alc. satd. in the cold with NH₃ gives 12 g. of the 1-amino compound, red-brown needles or leaflets with greenish luster from alc., m. 146–7°; 16 g. of this in 130 cc. concd. H₂SO₄ at 0° is slowly treated with 3 g. NaNO₂ in 45 cc. concd. H₂SO₄, stirred 10–5 min. longer, cautiously poured upon ice, treated with 12 g. Cu powder, heated on the H₂O bath until the decompn. is complete (some hrs.), filtered, and freed of Cu by repeated boiling with 3% HNO₃; there is thus obtained 14 g. of a yellow-brown powder (A); 5 g. of this boiled in 20 cc. C₆H₅N with charcoal deposits on cooling 1.2 g. dimethyl-2,1-anthraquinonefluorenone (3,4-phthalyl-5,8-dimethylfluorenone) (I), yellow-brown leaflets with intense green fluorescence, m. 266°. If 14 g. A is boiled out twice with 250-cc. portions of CS₂ there remains undissolved 7 g. 1-methylphenanthroanthraquinonefluorenone (II) as a light brown powder, volatilizes 370–40°, gives with alk. Na₂S₂O₄ a not very characteristic light brown vat

unchanged by boiling with Zn dust. The CS_2 ext. of A yields I when concd. to 0.25 its original vol.; with $\text{Na}_2\text{S}_2\text{O}_4$ on gentle warming I gives an intense wine-red vat. The mother liquors from I, evapd. to dryness and extd. with hot 10% NaOH, give on acidification small amts. of light brown flocks, probably of 1-hydroxy-2-p-xyloylanthraquinone; the residue (3.5 g.) m. 159° and consists of *a-p-xyloylanthraquinone*; with $\text{Na}_2\text{S}_2\text{O}_4$ on gentle warming it forms an intense emerald-green vat. II is easily obtained from I by fusing with 5 parts ZnCl_2 at 270° or by heating with concd. H_2SO_4 . I heated 45 min. with 8.5 parts powdered KOH gives *5-methylphenanthroanthraquinonecarboxylic acid* (III), red-brown flocks, analyzed as the *silver salt*; III is also obtained in 1.5-g. yield from 2 g. II heated 10 min. with 16 g. fused KOH at 230° .

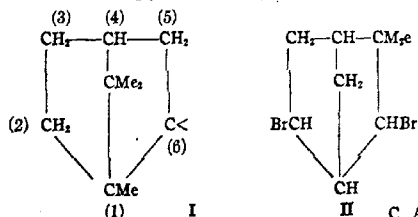


CHAS. A. ROUILLER

Camphene series. I. Reaction mechanism of the isoborneol \rightleftharpoons camphene rearrangement. HANS MEERWEIN AND KONRAD VAN EMSTER. Univ. Bonn. *Ber.* **53B**, 1815-29 (1920).—The difficulties and contradictions encountered when the assumption is made that tricyclene (A) is an intermediate product in the rearrangement of isoborneol (B) into camphene (C) had led M. to adopt Tiffeneau's suggestion that the radical I with bivalent C might be the intermediate product. This radical has now been obtained by the action of yellow HgO on camphor hydrazone; there is first formed a Hg compd. which has not yet been studied further but which, in view of the structure of the mercuriammonium compds., probably has the constitution $\text{C}_9\text{H}_{14}\text{CH}_2\text{C}$:

NNH_2HgOH ; on long heating in alc. suspension it decomps. into $\text{N}_2 + \text{H}_2\text{O} + \text{Hg} + \text{I}$ and the I under the conditions isomerizes almost exclusively into A, together with a little of an unsatd. hydrocarbon, probably C; this eliminates I as an intermediate product in the $\text{B} \rightleftharpoons \text{C}$ rearrangement. A having been made readily available by this method of prepn., the possible role which it plays in the rearrangement was again studied. Under the conditions producing an almost complete change of B into C (heating several hrs. at 100° with 33% H_2SO_4), A is practically unchanged (cf. also Lipp, *C. A.* **14**, 3237). A, then, is also excluded as a possible intermediate product in the rearrangement. The same thing was proved somewhat differently for the reverse reaction by studying the velocity of addition of org. acids to A and C, both of which thus yield esters of B; 1 mol. A or C was heated at 80° with 1.1 mols. $\text{ClCH}_2\text{CO}_2\text{H}$ and it was found that C reacts with appreciably greater velocity than A, so that the latter could not possibly be an intermediate product in the change of C into B or its ester. M. and van E., however, were able to show that the change of A into B or its ester does not consist of a simple rupturing of the ring between C atoms 2 and 6 but that the ring first opens between atoms 1 and 2 or 1 and 6, forming esters of the test. camphene hydrate (D) which then rearrange into esters of B; these expts. will be reported on in detail later. In agreement with this is the fact that the ring in A quite generally is ruptured with the greatest ease between these C atoms; thus, with H and Ni at $180\text{--}200^\circ$ A smoothly yields isocamphene, apparently first isomerizing into C. The quite rapid addition of Br to A leads to the formation of an oily dibromide, from

which, even on seeding, no crystals of pinene or camphene dibromide sep.; the primary addition product can, therefore, probably have only the structure II; whether the product actually has this structure or is at once further isomerized has not been detd.; one Br atom is easily removed by boiling alc. alkalis. If A in about 0.5 vol. cold dry Et₂O is treated with gaseous HCl until approx. 1 equiv. has been absorbed, there is obtained about 70% of a salt, fern-like crystals, m. about 125–7°, having a strong, markedly menthol-like odor; it is also obtained under the same conditions from C and is the true chloride of D or *camphene hydrochloride* (E). As a tert. chloride it is characterized by the extraordinary mobility of its Cl atom and the ease with which, by loss of HCl, it regenerates C; HCl begins to be split off shortly after the E is prepd. and the reaction seems to be catalyzed by acids; the HCl set free at the same time produces a gradual isomerization of the E into isobornyl chloride (F), m. 158°; as a result it has never yet been possible to obtain the E more than about 91% pure. On shaking with cold H₂O it is converted within a few hrs. into D; with alkalis the reaction is even more striking so that the E can be smoothly titrated in the cold with 0.5 N alc. KOH. The constitution of F is so well established that there is no doubt that it contains the camphor skeleton and is, therefore, a stereoisomer of bornyl chloride or pinene-HCl (G). Unlike E, F is hardly attacked by 0.5 N alc. KOH in the cold, but the Cl can be eliminated almost quant. by boiling 1 hr. with excess of 0.5 N alc. KOH, while under these conditions G is practically not attacked. It is, therefore, possible by a simple titration procedure to det. approx. quant. each component in a mixt. of E, F and G. This method was used to study the rearrangement of E into F. A prepn. containing 84.9% E and 13.0% F was found to contain only 79.9 and 16.0% E and F after standing 3 days; another sample with 86.0% E and 13.0% F contained after 14 days in a HCl atm. 64% E and 30.2% F; 4 g. of a prepn. with 91.1% E and 8.1% F heated 1.5 hrs. in a sealed tube at 140–50° gave a yellowish product, m. 103–8°, with 5.1% E and 83.0% F, the rest consisting entirely or partly of G; finally 25 g. of a prepn. like the preceding in 10 cc. Et₂O allowed to stand 5 days at 23° with 90 cc. MeOH satd. with HCl gave 18.4 g. of a product with 5.3% E and 93.0% F. Apparently the rearrangement does not go to completion but there is established an equil. involving E and F and possibly G. E and F, therefore, behave like tautomeric compds. The mechanism of these isomerizations has not yet been detd. with certainty; it is probable that there is a true intermol. shifting of atoms, *i. e.*, a direct change of place between the alkyl radical and the halogen atom. C obtained from B, and *vice versa*, is always optically inactive, whether or not the original material was active. The racemization may be brought about by the profound loosening of the mol. produced by the const. change corresponding to the tautomeric character of the esters of B and D, but it is not impossible that besides the main reaction $B \rightleftharpoons D \rightleftharpoons C$, there is a second reversible reaction, $D \rightleftharpoons A$, the racemization being produced through the sym. inactive A.



C. A. ROUHLER

Additions of aliphatic aldehydes to unsaturated compounds: a new synthesis of β -lactones (preliminary communication). HANS MEERWEIN. Univ. Bonn. Ber.

53B, 1829-35(1920).—Aliphatic aldehydes, insofar as they contain at least one H atom on the C adjacent to the CHO group, have to a striking degree the power to add to α,β -unsatd. ketones, esters and aldehydes (cf. C. A. 13, 1310). This additive ability of aliphatic aldehydes might well depend on their tautomeric character, which, to be sure, does not in general markedly manifest itself; all attempts, however, to obtain Na salts of them by the action of Na, NaOEt or NaNH₂ on their Et₂O solns. have resulted in the immediate formation of the corresponding aldols, even at -40° . That, nevertheless, they can be made to condense with unsatd. compds. under the influence of KOMe, sometimes with good yields, is explained by the fact that aldolization proceeds more slowly in alc. than in all other solvents because the aldehydes combine quite generally, with evolution of more or less heat, with alcs., forming hemiacetals of the general type $RCH(OH)OR'$; the reaction is reversible, so that the soln. always contains some free aldehyde. The 1,5-dialdehydes and ketone-aldehydes resulting from the addition reaction are smoothly converted by alc. alkali alcoholates, by an intramol. Cannizzaro reaction, into the isomeric β -lactones. The rearrangement is rapid (50% complete after 2 hrs. at 20° with 0.5 N alc. KOH). To obtain the lactones or their corresponding acids it is not necessary to isolate the intermediate addition products. α,α -Dimethyl- β -phenyl- γ -benzoylbutyraldehyde (19 g. from 30 g. PhCH:CHBz mixed with 30 g. Me₂CHCHO and 90 cc. MeOH, cooled to room temp., neutralized to phenolphthalein with KOMe, treated with 3.5 cc. of 10% KOMe and heated 5 hrs. at 40°), seps. from acetal in needles, m. $105-6^\circ$, seps. into its components a few degrees higher. α,α -Dimethyl- β,δ -diphenyl- δ -hydroxyvaleric acid (39 g. from 30 g. PhCH:CHBz, 30 g. Me₂CHCHO, 90 cc. MeOH and 2 g. K in 15 cc. MeOH heated 10 hrs. at $45-50^\circ$, then treated with 10 g. K in 75 cc. MeOH, allowed to stand 24 hrs., dild. with such an amt. of H₂O that the soln. remains clear after shaking, boiled 0.5 hr., cooled, poured into much H₂O, freed of non-acid constituents by repeated shaking with Et₂O and pptd. with dil. H₂SO₄), seps. from CHCl₃ in prismatic tables with 1 mol. solvent, from moderately dil. AcOH in rhombic prisms, m. $154-5^\circ$, converted at 200° into the lactone, needles from alc., m. $106-7^\circ$. α,γ,γ -Trimethyl- β -ethyl- δ -valerolactone (29 g. from 39.2 g. EtCH:CMcCHO, 57.6 g. Me₂CHCHO and 120 cc. MeOH allowed to stand overnight with 6 g. K in 75 cc. MeOH, treated with 2 g. more K in 25 cc. MeOH, heated 6 hrs. at 35° , then treated with 11 g. KOH in 200 cc. alc., heated 10 hrs. at 45° and 2 hrs. to boiling, freed from alc., treated with much H₂O, shaken with Et₂O and pptd. with acid (the HO acid at once goes over into the lactone), taken up in Et₂O, shaken with dil. soda, dried with CaCl₂ and distd.), is a mobile oil, $b_{17-8} 140^\circ$, $d_{16} 0.9892$, $n_D^{20} 1.46412$, easily volatile with steam, has a pleasant peppermint-like odor, is oxidized by KMnO₄ to α,α,α' -trimethyl- β -ethylglutaric acid, prisms from H₂O, m. $135-6^\circ$. The HO acid is so unstable that when an exactly neutralized aq. soln. is boiled alkali is set free and the lactone dists. over with the steam.

CHAS. A. ROULLER

Preparation of some esters of benzenesulfonic acid. ZOLTÁN FÖLDI. Fabrik "Chinoin," Budapest. Ber. 53B, 1836-9(1920).—Very satisfactory yields of the esters of PhSO₃H are obtained by treating a mixt. of PhSO₂Cl and the appropriate alc., with cooling and shaking, with 20-30% NaOH in small portions until the soln. is permanently alk., shaking several hrs., sepg. the 2 layers (after the addition of H₂O if necessary), washing the ester layer with H₂O, drying and distg. *in vacuo*. The following benzene-sulfonates were prepd. in this way: *Allyl*, colorless or faintly yellowish oil decomps. almost explosively when distd. under 15 mm. but small amts. (5 g.) can be distd., apparently with decompn., as the b. p. gradually rises from 150° to 170° under 10 mm. and an explosion occurs at the end of the distn.; heated in a test-tube, it decomps. vigorously at $160-70^\circ$; it shows $d_4^{16} 1.166$. β -Chloroethyl (A) (150 g. from 80 g. ClCH₂CH₂OH), $b_3 184^\circ$, $d_4^{16} 1.353$. β -Bromoethyl (65 g. from 82 g. BrCH₂CH₂OH), $b_{14} 185-7^\circ$,

d_4^{25} 1.575. β , β -Dichloroisopropyl (B) (55 g. from 65 g. $(\text{CICH}_2)_2\text{CHOH}$), b_p 200–5°, long needles from C_6H_6 , m. 50°, is extraordinarily resistant to sapon., being almost unchanged by long heating with 30% NaOH. By heating A and B 1 hr. with known vols. of 0.1 N alc. KOH, then titrating the unchanged KOH and the ionizable Cl it was found that whereas in A the sulfonic ester grouping is hydrolyzed about 3 times as rapidly as the Cl, in B both Cl atoms are hydrolyzed about 1.57 times as rapidly as the sulfonic ester grouping. Cf. following abstr.

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Alkylation of phenols with benzenesulfonic esters. Some new morphine ethers. ZOLTAN FÖLDI. Fabrik "Chinoin," Budapest. *Ber.* 53B, 1839–47 (1920).—From his expts. on the etherification of phenols with PhSO_2Me , PhSO_2Et and the esters described in the preceding abstr., F. finds that the allyl ester is by far the most reactive. The reactivity seems to depend upon the velocity of sapon.; the more readily and rapidly the sulfonic ester is sapond., the more energetically does it react with alkali phenolates. As for the substituents in the phenols, the same law holds as for methylation with Me_2SO ; substituents which increase the acidity of the HO group (halogens, NO_2 , etc.) hinder the reaction; negative substituents in the p -position seem to have a smaller hindering influence than in the o -position. In his expts., F. treated the phenol in EtOH or AmOH with the calcd. amt. of Na in the same alc. and boiled the soln. with the sulfonic ester. In this way he prepd. $\text{PhOCH}_2\text{CH}:\text{CH}_2$, $\text{PhOCH}_2\text{CH}_2\text{Cl}$, $\text{PhOCH}_2\text{CH}_2\text{Br}$, o - and p - $\text{O}_2\text{NC}_6\text{H}_4\text{OCH}_2\text{CH}:\text{CH}_2$, o - $\text{MeOC}_6\text{H}_4\text{OCH}_2\text{CH}:\text{CH}_2$, o - $\text{CH}_2:\text{CHCH}_2\text{OC}_6\text{H}_4\text{CO}_2\text{Me}$ and the following new ethers: *o*-chlorophenyl allyl ether (6 g. from 6.5 g. o - $\text{ClC}_6\text{H}_4\text{OH}$), b_p 118–20°, d_4^{25} 1.133, has an odor of carrots. From 22 g. o - $\text{C}_6\text{H}_4(\text{OH})_2$ are obtained 7 g. *pyrocatechyl diallyl ether*, b_p 138–9°, much less volatile with steam than veratrole, and the *monoallyl ether*, b_p 110°, d_4^{25} 1.091, markedly less volatile with steam than guaiacol. When 2.3 g. Na in 120 cc. alc. and 30.3 g. morphine are treated in the course of 1 hr. at 20–5° with 20 g. $\text{PhSO}_2\text{CH}_2\text{CH}:\text{CH}_2$, heated to 40° until the alk. reaction to phenolphthalein disappears (about 1 hr.), freed from any unchanged morphine in the usual way and the Et₂O soln. of the ether is evapd. and the residue, in the least possible amt. of alc., is exactly neutralized with alc. HCl and treated with Et₂O until there is only a faint turbidity, there is obtained 25 g. of *morphine allyl ether hydrochloride*, scales with 1 H₂O, m. 128–9° on rapid, 130–2° on slow heating, and (anhydrous) 152–3°. Free ether, seps. with 0.5 H₂O, m. 67–8°, $[\alpha]_D^{19}$ –85.89° (0.7079 g. hydrated HCl salt in 10.9404 g. H₂O). *Hydroiodide*, very faintly yellow crystals from H₂O containing HI, m. 225–6°. *Neutral sulfate*, from the base dissolved in the calcd. amt. of warm dil. H₂SO₄, long needles with 3 H₂O, m. in its H₂O when plunged into a bath at 120° but m. only 167–8° when heated in the usual way; its seps. from alc. in anhydrous crystals m. 172–3°; its aq. soln. is neutral to litmus and Me orange. *Acid sulfate*, from 1 mol. each of the base and dil. H₂SO₄, crystals from alc., m. 202–3°, reacts acid to Congo in H₂O. *Neutral phosphate*, from 3 mols. of the base and 1 mol. aq. H₃PO₄ evapd. to dryness in a desiccator, forms a slightly brown powder, m. 100°, from whose alc. soln. Me₂CO-Et₂O ppts. the primary *phosphate* (also pptd. by Me₂CO-Et₂O from 1 mol. each of the base and H₃PO₄ in aq. alc.), m. 186°, acid to Me orange and neutral to Congo in H₂O. *Neutral oxalate*, crystals with 0.5 mol. solvent, from alc., m. (air-dry) 130°, resolidifies and m. again about 203°; even when completely dried it shows a double m. p., 123° and 202–3°. *Morphine β -chloroethyl ether hydrochloride*, crystals with 1 H₂O, m. 150–1° and (anhydrous) 166–8°. Free base, seps. with 0.5 H₂O, m. 74–5° on rapid, 75–6° on slow heating, solidifies 80° and m. again 105° (gas evolution); anhydrous, it m. 118–20°. *Neutral sulfate*, needles from alc., m. 115–20° (foaming), resolidifies and m. again 235–40° (decompn.). *Primary phosphate*, crystals from MeOH-Me₂CO, m. about 110° (foaming). *Hydroiodide*, yellowish crystals from H₂O containing HI and MeOH, m. 212–3°. *Neutral oxalate*, needles from MeOH-Et₂O, m. 85–7°. In the hydrolysis of $\text{PhSO}_2\text{CH}_2\text{CH}_2\text{Br}$

with 1 mol. of 0.1 *N* alc. NaOH it was found that $\frac{1}{2}$ of the alkali was used in splitting off Br, which made it seem very likely that this sulfonic ester would not be well adapted to the etherification of phenols. An expt. with PhOH itself showed that some $\text{PhOCH}_2\text{CH}_2\text{Br}$ was indeed formed but in poor yield and accompanied by many by-products ($\text{PhOCH}_2\text{CH}_2\text{OH}$ and $\text{PhSO}_3\text{CH}_2\text{CH}_2\text{OH}$). Similarly with morphine there was obtained only a very impure *morphine β -bromoethyl ether hydrochloride*, m. 210–30°; free base, m. 135–6° (gas evolution), resolidified 139–40° and m. again 185–7°. Likewise the *morphine β,β' -dichloroisopropyl ether*, m. 147°, obtained by this method was impure in spite of repeated recrystn. and a const. m. p.; free base, m. 115°.

CHAS. A. ROULLER

Malonyl bromide and a synthesis of *peri*-acenaphthindandione. KARL FLEISCHER, HEINRICH HIRTEL AND PAUL WOLFF. Univ. Frankfurt a. M. *Ber.* 53B, 1847–52 (1920).—All the indandiones thus far prepd. by Freund and Fleischer's method (*C. A.* 14, 3661, and earlier papers) were doubly alkylated on C atom 2 of the hydrindene ring, as dialkylmalonyl chlorides were used in their prepn. Attempts to prep. the non-substituted derivs., starting from $\text{CH}_2(\text{COCl})_2$, failed on account of the instability of this chloride. In view of the apparent superiority of $(\text{COBr})_2$ over $(\text{COCl})_2$ for ring formations (*C. A.* 14, 3249) it was decided to try *malonyl bromide* (A) for the indandione syntheses. The A, a light yellow, heavy liquid with distinct green fluorescence, b₁₁ 55–7°, fuming strongly in the air and gradually turning brown on standing, was prepd. by passing through 40 g. $\text{CH}_2(\text{COCl})_2$ in ice the HBr evolved from 18 g. red P under 36 cc. H_2O and 180 g. Br and passed over asbestos wool laden with moist red P and through cold concd. H_2SO_4 ; the process was so regulated that the Br was used up in 4.5 hrs. and the mixt. was then allowed to stand 6 hrs. in the cold, freed from Br with Hg and distd. *in vacuo*. When to 15.4 g. acenaphthene in 75 cc. CS_2 and 30 g. AlCl_3 in a bath of warm water is added 25 g. A with const. shaking and, after the operation is completed (about 35 min.), the mixt. is heated 20 min. on the H_2O bath, decompd. with ice and HCl and steam distd. for 1 hr., and the dried granular black residue (22 g.) is extd. with 500 cc. dil. NaOH with gentle warming, dil. H_2SO_4 ppts. from the alk. ext. 4 g. *peri*-acenaphthindandione, yellow-brown rectangular columns from AcOH, changing color somewhat at 300° without melting, sol. in concd. H_2SO_4 with light yellow color and blue fluorescence. A similar expt. with $\text{CH}_2(\text{COCl})_2$ gave 1.4 g. material from which no cryst. product could be isolated. The indandione (1 g.) heated 6 hrs. at 150° with 3 cc. fuming HNO_3 (d. 1.5) and 1.5 cc. H_2O gave 0.2 g. mellophanic acid, m. 239–41°, and a naphthalenetetracarboxylic acid (B), needles which did not m. 300°, identical with that obtained by oxidation of acenaphthene-5-dimethylacetyl-6-carboxylic acid (*C. A.* 8, 663) and to which Bamberger and Philipp had assigned the structure $1,4,5,8\text{-C}_{10}\text{H}_4(\text{CO}_2\text{H})_4$ (*Ann.* 240, 155(1887)) without being able to prove its correctness exactly. The fact, however, that in the present work mellophanic acid was also isolated proves that the closing of the indandione ring by the action of $\text{CH}_2(\text{COBr})_2$ on acenaphthene occurs on the 2 *peri*-positions and hence that B. and P.'s structure for B is correct.

CHAS. A. ROULLER

Unsaturated bile acids. FR. BOEDCKER. J. D. Riedel A.-G. *Ber.* 53B, 1852–62(1920).—With acid dehydrating agents under the proper conditions, cholic acid (A) loses 1 mol. of H_2O , forming an unsatd. dihydroxycholenic acid, $\text{C}_{24}\text{H}_{46}\text{O}_4$, designated as *apocholic acid* (B). The ease with which it is formed indicates that of the three HO groups in A one is split off much more easily than the other two. Now, two of the HO groups in A occupy the same positions on the C skeleton as the two in desoxycholic acid (C) (Borsche, *C. A.* 13, 2356). If it is these two HO groups which remain intact when H_2O is split off from A, B should be simply an unsatd. C. It has not been possible to prove this directly on account of the unexpected resistance of B to reduction, but except for its unsatd. character B behaves in all respects almost exactly like

C; it forms with hydrocarbons, alcs., ethers, ketones, aldehydes and esters peculiar addition products analogous to those formed by C and designated by Wieland and Sorge "choleic acids" (C. A. 11, 257). Of nine such compds. of B, all but one combine in the same mol. proportion with the addendum as does C, the exception being camphor, which combines mol. for mol. with B but with 2 mols. C. The only difference in the chem. properties of these additive products is that those of B in some cases dissociate somewhat more readily than the corresponding C compds. The additive power of B is also retained to some extent by its Me ester. Finally, like C B forms a characteristic Mg salt. When 50 g. A are boiled 45 min. under a reflux with 8.5 g. $ZnCl_2$ in 150 cc. AcOH, poured into cold H_2O and nearly neutralized with soda and the pptd. acids are dissolved in hot dil. NaOH, cautiously repptd. with HCl, dried, powdered, stirred with 1.5 parts Et_2O , allowed to stand overnight, filtered (the filtrate on evapn. leaves about 5 g. of a yellowish resin which is easily sol. in dil. alkalis and NH_4OH and which instantly decolorizes $KMnO_4$ in cold dil. soda; it probably consists chiefly of more highly unsatd. bile acids), digested with 2 parts cold abs. alc. (which leaves undissolved about 4 g. A), concd. *in vacuo* and treated with xylene there is obtained 25 g. of 2B- $C_6H_5Me_2$ (see below). Recrystd. repeatedly from glacial or 75% AcOH it yields the *acetic acid compound*, B.AcOH, prisms, $[\alpha]_D^{20}$ 45.35° (alc.), stable for weeks in the air at room temp. but loses AcOH on heating (10% after 1.5 hrs. at 110–5° and 2.5% more at 130°) and then m. 170–1°. Free B, pptd. by HCl from solns. of the AcOH compd. in warm dil. alkalis, NH_4OH or soda, powder, m. 170–1°; it is obtained in purer state by treating 10 g. of the AcOH compd. in 50 cc. hot alc. with H_2O to incipient turbidity; on cooling the *alcohol compound* seps. in fine needles which quickly lose their alc. in the air and are heated a short time at 120–30° under 0.1–0.3 mm. The B now m. 173–4°, $[\alpha]_D^{20}$ 49.87° (alc.), at once decolorizes $KMnO_4$ in soda, violently reacts with Br in cold MeOH, forming a dibromide, has a faintly bitter taste, gives the Pettenkofer reaction, gives with $Ac_2O-H_2SO_4$ the same color phenomenon as C but to a more marked degree; its alkali salts are easily sol. and the solns. give plaster-like ppts. with Ba, Ca and Sr chlorides; the dil. NH_4OH soln. treated with $MgCl_2$ just up to the point where no ppt. is yet formed and then boiled yields a *magnesium salt* in fine needles; the *silver salt* is a gelatinous ppt. sepg. from an NH_4OH soln. warmed on the H_2O bath to expel the NH_3 as a finely granular heavy powder. *Addition compounds*: B, like C, forms no compds. with HCO_2H . *Butyric acid*, 2B. $PrCO_2H$, from B in hot satd. alc. soln. and $PrCO_2H$, needles, m. about 170°. *Palmitic acid* (2:1), fine needles from alc., m. 184–5°, $[\alpha]_D^{20}$ 43.7° (alc.), loses all its palmitic acid above 200° *in vacuo*. *Stearic acid*, fine needles from alc., m. 185–6°. *Benzene*, needles, m. 174–5°. *Xylene* (2:1), elongated 6-sided tables, m. 171–2°. *Naphthalene* (2:1), fine needles, m. 173–4°, $[\alpha]_D^{20}$ 41.20° (alc.), stable in the air and odorless. The *cryst. ethyl alcohol*, *ethyl acetate* and *acetone compounds* easily lose their addenda. *Benzaldehyde*, obtained by heating B with excess of BzH and then treating with ligroin, needles, m. 156°, stable in the air and odorless. *Camphor* (1:1), needles, m. 179–80°, $[\alpha]_D^{20}$ 43.80° (alc.). *Methyl ester* of B (24 g. from 30 g. B in 80 cc. MeOH satd. in the cold with HCl), thick prisms with $\frac{1}{2}$ MeOH, m. 83–4°, gradually weathers and m. (solvent-free) 88–90°; recrystd. from 75% AcOH it gives an *acetic acid compound* (1:1), yellow prisms, m. 87–8°.

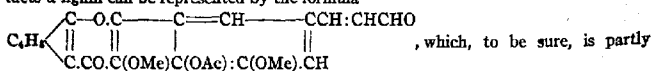
CHAS. A. ROUILLER

* *Lignin and lignin reactions. II. PETER KLASON. Ber. 53B, 1862-3 (1920); cf. C. A. 14, 3229.*—By the sulfite process all of the lignin can be extd. from the wood of the Scotch pine, birch, beech, oak, linden, aspen, alder and saw and from the solns. can be obtained yellow cyclic β -naphthylamine salts of practically the same appearance and properties and by the same method as from the pine. The N and S content of all these salts is about the same (N 1.82–2.40%, S 4.84–5.43), and while the lignins in all these different kinds of woods are certainly not identical it may be

concluded that all have a structure of the same type. The lignin in herbaceous plants can also be dissolved out by the sulfite process and the solns-likewise yield yellow cyclic aryl-ammonium salts, but they have a materially different compn., as will be described in detail later.

CHAS. A. ROUHLER

Constitution of the lignin of pine wood. PETER KLASON. Forstakademie, Stockholm. *Ber.* 53B, 1864-73(1920).—That part of the lignin which contains an acrolein group and whose lignosulfonic acid gives cyclic arylammonium salts is designated acrolein-lignin or α -lignin; it is identical with the Ca lignosulfonate pptd. by CaCl_2 . But there is also another lignin in wood whose Ca sulfonate is not pptd. by CaCl_2 , gives no cyclic ammonium salt but contains a CO_2H group; this is called carboxyl-lignin or β -lignin. The coniferyl alc., in which form the acrolein complex is present in α -lignin, represents only about 0.5 of the α -lignin mol. The analyses of the Ca sulfonate by K. (*Svensk. Kem. Tid.* 1917, 8), and by Hönig and Spitzer (*C. A.* 13, 131) agree remarkably well, especially for amorphous substances of high mol. wt., and correspond to the formula $\text{C}_{40}\text{H}_{40}\text{O}_{12}\text{S}_2\text{Ca}$, or $\text{C}_{40}\text{H}_{40}\text{O}_{12}$ for the α -lignin itself. For reasons stated below it is believed that this formula should be halved ($\text{C}_{20}\text{H}_{20}\text{O}_6$ or $\text{C}_{20}\text{H}_{22}\text{O}_6$); K. in the present paper adopts $\text{C}_{20}\text{H}_{20}\text{O}_6$. As has long been known, AcOH and HCO_2H are formed from pine wood in the sulfite process; 45 g. (dry wt.) of wood boiled with the sulfite acid until all the lignin had been dissolved out gave 0.945 g. AcOH ; when the soln., freed from AcOH , was heated 12 hrs. on the H_2O bath with H_2SO_4 to invert it, 0.21 g. more AcOH was obtained, or a total of 1.155 g. acid, of which about 10% was HCO_2H , while the calcd. amt. of AcOH from the 8.5 g. α -lignin in the 45 g. wood (see below), on the assumption that the α -lignin contains one hydrolyzable Ac group, is 1.28 g. Pine wood powder (37 g. dry wt.) inverted 24 hrs. on the H_2O bath with 400 cc. N H_2SO_4 gave 2.1 g. AcOH per 100 g. wood. Assuming that the Ac group is completely split off the AcOH formation equals 2.86% of the dry wt. of the wood. As about the same amt. of acid from the lignin is obtained by the dry distn. of the wood the formation of the acid in this case must depend on the splitting off of the Ac group by means of the steam in connection with the high temp. The acrolein-lignin of the wood therefore has the compn. $\text{C}_{20}\text{H}_{20}\text{O}_7$. The sulfonic acid of this lignin is completely pptd. by $\beta\text{-C}_{10}\text{H}_7\text{NH}_2\text{HCl}$. The lignin completely extd. from 38.93 g. (dry wt.) of the wood of an 80-yr.-old pine gave 10.5 g. cyclic salt = 7.4 g. α -lignin = 19% of the wt. of the wood. K. by means of 70% H_2SO_4 (*Ver. Zellstoff- u. Papier-Chem.*, Hauptvers. 1908) and Hägglund with concd. H_2SO_4 (*Arch. Kemi.* 1918, 11) found 28% lignin in pine wood, a figure which must be increased to 30% to allow for the AcOH split off. The wood, therefore, contains, in round numbers, 68% carbohydrates, 30% lignin and 2% of other substances, and the lignin consists of 63% α - and 37% β -lignin. The cyclic β -naphthylamine salt contains, as the mean of detns. made on different fractions and preps., 2.02% N and 5.31% S, whence, on the basis of the above formula for α -lignin, its compn. is $\text{C}_{20}\text{H}_{20}\text{O}_8\text{SN}$, i. e., it contains only one acrolein group. On treatment with alk. Me_2SO_4 at room temp. and subsequent neutralization and pptn. with alc. the salt gives a compd. with 19.7% MeO , while the original salt has 12.87% MeO , i. e., 2 MeO and 1 free HO group; as this HO group is acetylated in the wood itself, the α -lignin in wood has no free HO group. The methylated salt does not ppt. glue, while the non-methylated salt does; the HO or AcO group must, therefore, be in the coniferyl-aldehyde nucleus. From the above qual. and quant. facts α -lignin can be represented by the formula



hypothetical. α -Lignin would then have a structure of the flavonol type. The residual salt obtained by Hönig and Spitzer by fractional pptn. of the Ba salt of ligno-

sulfonic acid, which they assigned the formula $C_{27}H_{37}O_{15}S \frac{Ba}{2}$ is probably a compd.

of lignosulfonic acid with a carbohydrate; when the lignosulfonic acid is completely pptd. from the sulfite liquor with β - $C_{10}H_7NH_2 \cdot HCl$ in HCl soln. and the filtrate is heated 12 hrs. on the H_2O bath the soln. again gives a small amt. of the yellow cyclic salt with $C_{10}H_7NH_2 \cdot HCl$. From the compn. of pine wood as given above and the relative amts. of α - and β -lignin, and assuming that the 2% of "other substances" contain 60% C and 10% H, the compn. of β -lignin can be calcd. to correspond to the formula $C_{15}H_{13}O_5$. When the α -lignosulfonic acid is just pptd. from the sulfite liquor with α - $C_{10}H_7NH_2 \cdot H_2SO_4$ and the filtrate is neutralized with chalk, concd. and treated with $MeOH$ there is obtained a dark green salt which, after resolution and repptn., has the compn. $C_{15}H_{13}O_5SCa$ (S 6.26, Ca 7.86%), with one MeO group; hence it probably contains both a sulfonic and a carboxyl group. The simplest assumption is that while the α -lignin has an acrolein group, $RCH:CHCHO$, β -lignin has an acrylic acid grouping $RCH:CHCO_2H$. In the wood this CO_2H is naturally not free but is undoubtedly combined with the carbohydrates. As the simpler carbohydrates, the pentosans, can in great part, even if with difficulty, be extd. from the wood with H_2O alone, this lignin must, for the most part at least, be combined with the cellulose. Presumably that is also the case with the α -lignin. From the above, in the complete extn. of lignin from 1 kg. pine wood 79.1 g. SO_2 and 34.6 CaO should combine with the lignin. The results of tests in the industry show that in a hard boiled mass about 76 g. SO_2 and 32 g. CaO are taken up.

CHAS. A. ROULLER

Synthesis of β -keto bases from amine salts, formaldehyde and cyclohexanone. C. MANNICH AND R. BRAUN. Univ. Frankfurt a. M. Ber. 53B, 1874-80(1920); cf. C. A. 12, 684.—It has been found that cyclic ketones as well as the aliphatic ketones condense with amine salts and $HCHO$ to form β -keto bases. Thus when 49 g. cyclohexanone (A), 9 g. $HCHO$ soln. and 9 g. $NHMe_2 \cdot HCl$ are warmed reaction soon sets in and, without further heating, proceeds to completion with vigorous boiling. After cooling, 50 cc. H_2O is added to the homogeneous mixt., the excess of A is drawn off or extd. with Et_2O and the soln. concd. *in vacuo*, giving about 85% of 2-dimethylaminomethylcyclohexanone hydrochloride (B), hygroscopic scales from $EtOH \cdot Me_2CO$ (1:14), m. 152° ; picrate, light yellow needles, m. 149° ; perchlorate, stout crystals, m. 156° ; chloraurate, yellow prisms, m. 132° ; free base, b_{11} about 100° , changes within 8 days into higher boiling products; oxime hydrochloride, deliquescent columns from $EtOH \cdot Me_2CO$ (1:20); cyanohydrin, from a concd. aq. soln. of B and KCN, broad needles from very dil. alc., m. 55° ; the methiodide is so unstable that it could not be obtained pure, its solns. decomp. at room temp. with sepn. of an oil and yielding on evapn. in a desiccator $NMe_2 \cdot HI$; among the N-free decompn. products is 2-methylenecyclohexanone (C). Oxidation of the base with $KMnO_4$ or HNO_3 gives adipic acid. From 10 g. of the base in 80 cc. Et_2O and 10 g. Al shavings activated with alc. $HgCl_2$ treated in the course of 5 hrs. with 10 cc. H_2O is obtained almost quant. 2-dimethylaminomethylcyclohexanol, oil, b_{11} 108° ; hydrochloride, hygroscopic scales, m. 180° ; acetate, from the alc. boiled 1 hr. with $Ac_2O \cdot NaOAc$, b_{11} 136° (hydrochloride, hygroscopic, m. 141°); benzoate, viscous oil (hydrochloride, needles, m. 220° , is a very powerful local anesthetic but at the same time quite toxic). When 34 g. $NH_2Me \cdot HCl$, 95 g. formalin and 196 g. A are heated under a reflux and the product is freed from the excess of A with Et_2O , evapd. almost to dryness and treated with an ice-cold soln. of 20 g. $NaOH$ and the pptd. soft mass is allowed to stand in Et_2O in the ice chest overnight there seps. 6 g. of a cryst. base (D), m. 172° ; the mother liquors on fractionation *in vacuo* yield C, considerable more D and 2-hydroxymethylcyclohexanone ether (E), $(CH_2CH_2CH_2CH_2CO \cdot CHCH_2)_2O$. D is bis[cyclohexanonyl-2-methyl]methylamine,

needles from alc.; hydrochloride, very hygroscopic; chloroaurate and -platinate, crystals; picrate, yellow needles from alc., m. 175°; methiodide, quadratic crystals from H₂O, m. 144°. C is an oil of a powerful odor, b₁₃ 65°; semicarbazone, scales from alc., m. 195°, decolorizes 2 atoms of Br in CHCl₃. E, which is also formed as a by-product in the prepn. of B if the temp. is raised too high, seps. from alc. or Et₂O in scales, m. 149°; bisphenylhydrazone, crystals from xylene, m. 191°. A (38.4 g.), 17.4 g. formalin and 2.7 g. NH₄Cl when boiled and, after the reaction is over, treated with 80 cc. H₂O and evapd. in vacuo give tris(cyclohexanonyl-2-methyl)amine hydrochloride, stout crystals from Me₂CO, m. 110°; free base, scales from Et₂O, m. 119°. CHAS. A. ROULLER

Relation of retene to resin acids, and hydrogenated retenes. ARTTURI J. VIRTANEN. *Helsingfors. Ber.* 53B, 1880-9 (1920).—V. briefly reviews earlier work done on the relation between retene and the resin acids. He believes that in order to det. whether hydrogenated retenes or their Me homologs and, if so, which of them, are obtained from resin acids it is important to prep. the different hydrogenated retenes and det. their properties; it was for this reason he carried out the present investigation. Dihydroretene (6 g. from 10 g. retene in 75 cc. boiling dry AmOH treated in the course of 2 hrs. with 5 g. Na, then poured hot into H₂O), leaflets from EtOH, m. 64-5°, b₁₈ 188-90°, forms no picrate, gives retenequinone in good yield with CrO₃-AcOH. Tetrahydroretene, obtained, together with 1 g. of the dihydro compd., in 7-g. yield from 10 g. retene and 9 g. Na, is a yellow-white oil, b₁₈ 180-3°, d₄²⁰ 1.0057, n_D²⁰ 1.5606, is apparently nitrated by hot concd. HNO₃, slowly sol. in concd. H₂SO₄ with bright red color turning to dark red and finally black-green on warming and remaining clear on diln. with H₂O. Hexahydroretene (4.8 g. from 6 g. retene, 7 g. fuming HI (d. 1.96) and 3 g. red P in a sealed tube filled with CO₂ heated in the course of 3 hrs. to 190-200° and kept 10 hrs. at that temp.), b₁₈ 175-7°, has a slight blue fluorescence and a faint, not unpleasant odor, unattacked by cold concd. HNO₃, nitrated on heating, sol. in concd. H₂SO₄ with deep blue color changing to brown-black on heating, d₄²⁰ 0.9802, n_D²⁰ 1.54770. Octahydroretene, from 6 g. retene, 7 g. HI and 3 g. red P heated to 240° in 4 hrs. and kept 8 hrs. at that temp., b₁₈ 163-5°, has a rather pleasant odor, not attacked by cold but nitrated by hot HNO₃, sol. in concd. H₂SO₄ with red-brown color, deep red by transmitted light, turning black-green on heating, d₄²⁰ 0.9578, n_D²⁰ 1.53020. Decahydroretene (2 g. from 6 g. retene, 7 g. HI and 3 g. red P heated to 285° in 4 hrs. and kept 10 hrs. at that temp.), b₁₈ 155-8°, smells of petroleum, nitrated by hot HNO₃, slowly sol. in H₂SO₄ with brown color. d₄²⁰ 0.9342, n_D²⁰ 1.51501. Dodecahydroretene (from 3 g. retene, 14 g. HI and 5 g. red P heated to 260-70° in 4 hrs. and kept at that temp. 10 hrs.), b₁₈ 148-50°, has a faint pleasant odor, very stable towards hot HNO₃, slowly sol. in H₂SO₄ with yellow color changing to brown-green on heating, d₄²⁰ 0.8985, n_D²⁰ 1.48510. CHAS. A. ROULLER

Anhydrides of higher aliphatic fat acids. III. D. HOLDE and H. SMOLEKUS. *Ber.* 53B, 1889-97 (1920); cf. C. A. 15, 251.—It has already been shown, in connection with the suggested possibility of using the anhydrides of the higher fatty acids instead of the glyceride fats for food purposes, that they are absorbed by the intestine, and from an oleic acid thoroughly purified by vacuum distn. was obtained an anhydride, which, used for quite a long time as a salad oil, fulfilled all requirements as to taste and lubricity, but when employed in frying potatoes acquired a sharp taste suggesting some decompn., probably produced at the higher temp. by the H₂O in the potatoes. As very little is given in the literature about these anhydrides except their m. ps. and a few solubilities, it seemed of interest to investigate their methods of prepn. and their properties somewhat more closely. That they have a certain tendency to decomp. as pointed out in the earlier paper, is confirmed by the fact that the linseed oil acid anhydrides prepd. by Albitzky's method (heating the pure acids with an equa. wt.

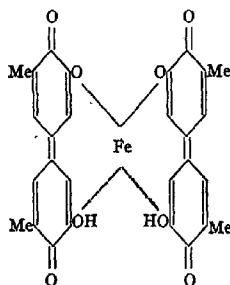
of Ac_2O 6 hrs. at $150-60^\circ$) washed with steam to disappearance of the acid reaction to Me orange in the condensed H_2O become wholly sol. in dil. aq. soda; of a sample so treated, when shaken in petr. ether with a slight excess of cold 0.05 *N* alc. NaOH, then washed with 50% alc. to remove the soaps, only 13.6% remained in the petr. ether as unchanged anhydride (or as Et ester?). Again, the yields of anhydrides obtained by the Albitzky method cannot be detd. by titration with 0.1 or 0.05 *N* alc. NaOH because there apparently takes place, not instantly, to be sure, but gradually, a half-esterification of the anhydride according to the equation $(\text{RCO})_2\text{O} + \text{EtOH} + \text{NaOH} = \text{RCO}_2\text{Et} + \text{RCO}_2\text{Na} + \text{H}_2\text{O}$. The very large excess of Ac_2O used by A. is apparently unnecessary. When 40 g. olein (Motard) was heated 4-5 hrs. at $160-60^\circ$ in a sealed tube with 43.5 g. Ac_2O , freed from Ac_2O and AcOH by heating under 15-20 mm. up to 125° (an aq. ext. of the residue no longer reacted acid to Me orange) and titrated in $\text{C}_2\text{H}_5\text{-EtOH}$ with 0.05 *N* NaOH in 96% alc. it showed an apparent content of 63.5-70% free oleic acid; 100 g. oleic acid heated 1.5 hrs. at $150-60^\circ$ under a reflux with 20 g. Ac_2O gave a product with apparently 62.5% free oleic acid; 150 g. of the same oleic acid heated 3-4 hrs. at $150-5^\circ$ under a reflux with 75 g. Ac_2O yielded a product apparently containing 55-56.3% free oleic acid. When the titrated soln. is dild. with H_2O until the alc. becomes 50%, there can be obtained from the C_2H_5 layer, treated with petr. ether, a mobile oil of ethereal odor remaining clear at low room temp. and doubtless consisting of Et oleate. Anhydrides from olinite fat acids (prepd. from the dry K salts and COCl_2) when shaken with 60% alc. or in $\text{C}_2\text{H}_5\text{-EtOH}$ showed an apparent free oleic acid content of 64-9%. While the free acids, such as from linseed oil and rape oil, and also oleic acid are still sol. in 72% alc. and the pure anhydrides are hardly sol., no sufficiently sharp method of sepn. can be based on these differences in soly. owing to the influence exerted by the free acids on the soly. of the anhydrides; in stronger alc. (96 or 85%) these influences are even more pronounced. Nor can the anhydrides be sepd. from the non-anhydridized acids by distn. in the vacuum of a H_2O pump, evidently because the anhydrides decomp. The only method of sepn. that remains consists in treatment with solid or aq. soda (see following abstr.).

IV. D. HOLDE AND IDA TACKER. *Ibid* 1898-1907.—Only the anhydrides of the mixed acids of liquid fats (linseed and rape oils and Motard olein) were used in the present work. They were prepd. by the Albitzky method but in general with a smaller excess of Ac_2O than used by him; the yields are apparently not diminished by cutting down the amt. of Ac_2O to 3.5 times the calcd. and it probably can be reduced still further. It also seems that heating under a reflux may be sufficient and that the use of sealed tubes can be avoided. The products were purified by removing most of the impurities by distn. *in vacuo* and the rest with solid powdered or 5% aq. soda. The anhydrides so obtained were, in contrast to the liquid fats from which they were prepd., at 18° of a salve-like or semiliquid consistency (in the case of those from rape oil partly cryst.) and became liquid at a somewhat higher temp. (23°); when liquefied they retain, in contrast to the Et esters, the same viscous oily consistency and slight volatility as the glyceride fats. The indices of refraction are about the same as those of the glycerides and higher than those of the free acids. That they are half-esterified by alc. NaOH, as indicated in the preceding abstr., was confirmed by titration and examn. of the titration product. The purity of the anhydrides was shown by detns. of the sapon. no. with boiling 0.5 *N* alc. KOH, and the absence of mixed acetic anhydrides by mol. wt. detns. and by the negative caodyl test. The quant. details of a number of expts. are reported.

C. A. ROULLER

Chief constituent of Japanese lac. VII. Urushiol monomethyl ether and the mechanism of the oxidation of urushiol. RIKO MAJIMA AND GYIARO TAKAYAMA. *Ber.* 53B, 1907-18(1920); cf. *C. A.* 10, 2875.—From 20 g. urushiol (A) in an equal amt. of abs. alc., 1.5 g. Na in 30 cc. alc. and 7.3 g. Me_2SO , heated 1 hr. on the H_2O

bath, freed from the alc. by distn., treated with H_2O , extd. with Et_2O , dried with Na_2SO_4 and distd. under about 0.2 mm. was obtained about 12 g. oil, b. about 210° (260 g. total yield from 370 g. A); 250 g. of this on repeated fractionation gave 4 fractions (about 208 g.) $b_{0.15}$ $172-200^\circ$ (chiefly $183-8^\circ$), d_4^{25} 0.9515-0.9606, Me (as MeO by the Zeisel method) 3.78, consisting largely of *monomethylurushiol* (B); in Et_2O with H and Pt this gives *monomethylhydrourushiol* (C), needles from MeOH, m. $44.5-5.0^\circ$, gives with FeCl_3 in alc. a greenish blue color, in H_2O a yellowish brown ppt. gradually becoming red-brown. C can also be obtained in 1.5-g. yield from 3 g. dimethylhydrourushiol (D) boiled 5 hrs. with 13 cc. HI (d. 1.7); only with boiling HI of d. 1.98 or by heating 2 hrs. at 180° with HBr (d. 1.78) could complete demethylation be effected. *Acetate* of B, leaflets from dil. MeOH, m. $45.5-6.5^\circ$. 2,3- $\text{HO}(\text{MeO})\text{C}_6\text{H}_3\text{Me}$ (E) (2 g.) in 40 cc. of cold 88% alc. treated with 4.8 g. FeCl_3 in 40 cc. H_2O , dild. after 1 hr. with H_2O to 600 cc. and allowed to stand overnight in the ice chest gave 1.5 g. 3,3'-dimethyl-5,5'-dimethoxy-4,4'-diphenoquinone (F), $[\text{O}:\text{C}_6\text{H}_3\text{Me}(\text{OMe})] = 1$, dark violet needles from abs. alc., m. $202-3^\circ$, requires 1 mol. SnCl_4 when titrated to complete decolorization in much almost boiling alc. in a CO_2 atm.; 2 g. suspended in 100 g. AcOH and treated with 2 g. Zn dust in small portions gives 1.9 g. of the *quinol*, colorless crystals from AcOH, m. $188.5-9.5^\circ$, repts. the quinone from alc. with FeCl_3 , mol. wt. in boiling Me_2CO 264-70; 1 g. heated 3 hrs. at 150° with 5 cc. HBr (d. 1.48) yields 3,3'-dimethyl-4,4',5,5'-tetrahydroxydiphenyl, crystals from AcOEt, darkens 220° , m. $230-1^\circ$ (decompn.) gives with FeCl_3 in alc. a blue color changing to violet-black, in H_2O a black ppt.; *tetraacetate*, needles, m. $193.5-4.5^\circ$. 3,3'-Dimethyl-4,4',5,5'-tetramethoxydiphenyl (G), from 1.5 g. of the quinol in 2.5 g. alc. heated 5 hrs. at 120° with 0.3 g. Na in 4 cc. alc. and 2.5 g. MeI, leaves from dil. alc., m. $102-3^\circ$. 2,3- $(\text{HO})_2\text{C}_6\text{H}_3\text{Me}$ (H) (2 g.) in 250 cc. cold H_2O treated in the course of 1 hr. with 5.25 g. FeCl_3 in 100 cc. H_2O and stirred 20 min. longer gives 1.6 g. of a *substance*, $(\text{C}_{12}\text{H}_{10}\text{O}_4)_2\text{Fe}$, as a blue-black ppt. indifferent towards NaOAc, sol. in alkalis with dark green color, easily reduced in AcOH with Zn dust, the colorless soln., on evapn. *in vacuo* in CO_2 and boiling 3 hrs. with Ac_2O giving G; the compd. is assigned the structure:



In the same way, 1 g. hydrourushiol¹ in 75 cc. cold alc. with 1 g. FeCl_3 in 250 cc. H_2O gives 0.75 g. of a *compound* $(\text{C}_6\text{H}_7\text{O}_4)_2\text{Fe}$ as a blue-black ppt. C similarly oxidized gives a *diphenoquinone*, red-brown cryst. ppt., m. $120-2^\circ$, reduced by Zn dust in AcOH to the *quinol*, m. $80-1.5^\circ$. Finally, 0.1 g. E with laccase in 20 cc. alc. and 40 cc. H_2O treated with air becomes orange, then red-brown, and finally deposits black-violet needles of F (the reaction is complete in 10 hrs.). H treated 1.5 hrs. in H_2O with air practically does not change but on addition of laccase gradually gives a brown ppt. which does not m. 280° and becomes dark brown in alc. with FeCl_3 ; with Zn dust in AcOH it yields a yellow powder m. $150-60^\circ$ which is apparently the impure *tetraacetate*.

oxyditolyl. These facts confirm M.'s conclusion that A is an analog of H, viz., 2,3-(HO)₂C₆H₂C₁₀H₁₇.

CHAS. A. ROUILLER

The relations between the dimeric ketenes and 1,3-cyclobutanedione and its derivatives. G. SCHROETER. Tierärztl. Hochschule Berlin. *Ber.* 53B, 1917-25 (1920); cf. C. A. 11, 2776; Staudinger, C. A. 14, 3423.—There is nothing in the Staudinger paper which speaks for the view that the dimeric ketenes are 1,3-cyclobutanediones, but there are very important facts against such a view. He has no proof at all that his two camphoketenes are really *cis-trans* isomers. The great difference in their optical rotations is contrary to such an isomerism and points to structural isomerism. Brühl, from observations with the FeCl₃ reaction, concluded that camphocarboxylic esters in C₆H₆ are present in the keto form and on addition of Na change into an enol form. Schroeter has now found for Me camphocarboxylate $[\alpha]_D^{20}$ 18.40° as the mean of a large number of detns. in C₆H₆ solns. at concns. from 0.3 to 3%. This may be taken as the value for the true keto form. In other solvents the keto-enol forms are in equil., $[\alpha]_D^{20}$ being 59.58°, 59.00°, 54.39°, 62.66° and 62.33° in alc., AcOEt, Et₂O, Me₂CO and CHCl₃, resp. If an equiv. of Na is added to the C₆H₆ soln., the now fully enolized soln. shows $[\alpha]_D$ 157.9°. This and other studies on the rotation of keto-enol isomers of the camphor series which are recorded in the literature lead to the conclusion that Staudinger's compds. may also well be keto-enol isomers.

CHAS. A. ROUILLER

Preparation of active hydrogenation metals (BROCHET) 13. Preparation of active hydrogenation metals in the midst of the liquid to be treated (BROCHET) 13. Splitting off of halogen from some organic compounds (HEDELIUS) 2. Reactive acid liquor from olefinic gases for alcohol manufacture (U. S. pat. 1,365,043) 22. Ketones from cracked gasoline (U. S. pat. 1,365,053) 22.

Benzoic acid. J. B. SENDERENS. U. S. 1,365,956, Jan. 18. Benzoic acid is formed by oxidation of toluene with a mixt. of H₂SO₄ and MnO₂ at a temp. of 60-70°.

Benzanthrone. L. C. DANIELS. U. S. 1,365,024, Jan. 11. Impure benzanthrone which may contain anthraquinone and resinous impurities is purified by dissolving it in a heated solvent such as chlorobenzene or other halogenated benzene or toluene derivs., sepg. the soln. from undissolved impurities and cooling the soln. to effect sepn. of the benzanthrone.

Producing toluene from xylene. A. S. RAMAGE. U. S. 1,365,840, Jan. 18. Toluene is produced from xylene by the action of H at a temp. of about 700° in the presence of Fe₂O₃ as a catalyst. Other similar dealkylations may be effected by the same method.

Esters from unsaturated hydrocarbons. C. ELLIS AND M. J. COHEN. U. S. 1,365,050, Jan. 11. A material such as olefins from petroleum still gases and vapors containing olefinic hydrocarbons is treated with H₂SO₄ of about 1.8 sp. gr. and the resulting product is caused to react with Ca(OAc)₂ and distd. in order to produce a mixt. of acetic esters. U. S. 1,365,051 relates to mixed esters such as acetic or formic esters produced from olefins of cracked petroleum and adapted for use with pyroxylin as solvents. U. S. 1,365,052 relates to the production of mixed esters adapted for use as pyroxylin solvents by direct combination of a fatty acid such as glacial HOAc with olefinic hydrocarbons such as produced by cracking petroleum in the presence of a catalyst, e. g., H₂SO₄.

Acetic ester mixture. C. ELLIS. U. S. 1,365,049, Jan. 11. A mixt. consisting largely of propyl acetate and containing also ethyl and butyl acetates, b. principally below 110°, and adapted for use as a solvent in airplane varnishes is prepd. by sulfation and esterification of petroleum still gases.

Separating alcohols from sulfuric acid. C. ELLIS. U. S. 1,365,046, Jan. 11. A solvent such as C_6H_6 which dissolves alcs. but not H_2SO_4 is used for sepgg. alcoholic material (such as obtained from cracked gasoline, H_2SO_4 and H_2O) from associated H_2SO_4 .

Purifying alcoholic material. M. J. COHEN. U. S. 1,365,047, Jan. 11. Alcoholic material such as derived from olefins, H_2SO_4 and H_2O is purified by distn. in the presence of a small quantity of H_2SO_4 , which serves to remove residual olefinic material and produce a colorless distillate.

Separating alcohols from hydrocarbons. C. ELLIS and M. J. COHEN. U. S. 1,365,048, Jan. 11. A mixt. containing alcs. and hydrocarbons, such as obtained from olefins, H_2SO_4 and H_2O , is treated with 1.57 sp. gr. H_2SO_4 in order to dissolve the alc. and effect sepn. from the hydrocarbons. The H_2SO_4 soln. of alcs. may then be dild. with H_2O to sep. most of the alcs. and the remaining portion may be recovered by distn.

Dinitrophenol. NORSK HYDRO-ELEKTRISK KVÆLSTOFAKTIESELSKAB. Brit. 153,265, Oct. 28, 1920. Phenol is nitrated at 95° with dil. HNO_3 which is fitted for further use by addition of strong acid from a N oxides absorption tower. A suitable app. is specified.

Phthalic anhydride. SGLDEN CO. Brit. 153,252, Feb. 16, 1920. Phthalic anhydride is obtained substantially pure in the form of colorless needles, melting above 130° . It may be prepd. by passing naphthalene vapor and air at $350-550^\circ$ over a catalyst such as Mo oxide, and purifying the resultant crude phthalic anhydride by sublimation in the app. shown. A suitable app. is specified.

Hydrogenation of organic compounds. R. LESSING. Brit. 152,740, July 15, 1919. In a process of hydrogenating oils and other org. compds. in which $Ni(CO)_4$ is employed as the source of the catalyst as described in 18,998, 1912, (C. A. 8, 589) excess of CO in the hydrogenator is obviated by sepgg. the carbonyl from the volatilizer gases by means of an absorbent before introducing the carbonyl into the hydrogenator. Thus, the volatilizer gases are passed through a scrubber or scrubbers packed with porous material impregnated with an absorbent such as oil, or filled with "activated" charcoal, and the gases stripped of their carbonyl contents are returned with or without enrichment with CO to the volatilizer for the treatment to be repeated; by which means if H_2O vapor is employed, pure H may be eventually obtained. The absorbed $NiCO$ is recovered by passing the H required for hydrogenation through the absorber, or through a second scrubber fed with the oil that runs away from the absorber; or the satd. charcoal may be suspended in the material to be hydrogenated, or carried into it by means of the hydrogenating gas. Birchwood charcoal previously dried by heating in H is advantageously employed.

Pyrogenic reactions. F. FISCHER. Brit. 152,960, Oct. 22, 1920. In carrying out org. reactions at high temps., the deposition of solid C on metallic parts of the app. is prevented by coating the metal with Sn or a Sn alloy. The Sn layer also acts as a catalyst. The production of benzene and toluene from cresol by treatment with H at 800° in an app. consisting of tinned Fe tubes is given by way of example.

11—BIOLOGICAL CHEMISTRY

HATTIE L. HEFT, EDGAR G. MILLER, JR., AND WILLIAM J. GIES

A—GENERAL

FRANK P. UNDERHILL

Amylolytic enzymes in the animal body with special reference to maltase. SHUNGO OSARO. Tohoku Univ. Sendai. *Tohoku J. Exp. Med.* 1, 1-37(1920).—One % starch in normal saline was used as a substrate in the detn. of amylase and the copper reduc-

tion method of Pavy-Kumagawa-Suto to det. the reducing sugar formed. In the detn. of maltase, O. used a 2.5% maltose normal saline soln. and considered the decrease in rotation as a measure of the dextrose formed. He withdrew samples at various intervals and freed them from enzymes by treatment with colloidal iron. The organs were macerated in normal saline with sand and the clear supernatant liquid, after centrifugation, used. The series includes material from dogs, cats, rabbits, guinea pigs, cattle, hogs and a human body. Maltase occurs in greatest quantity in the upper parts of the small intestine in all cases and does not vary markedly lower down the small gut in the cat and dog, but is less in the ileum of the rabbit and pig and next in order is the blood serum and pancreas. Then in order of decreasing maltase content come the liver and muscles. The blood serum of the pig is higher in maltase than that of the dog, which is higher than the other animals. The blood and lymph diastase of the dog is much increased after pilocarpine injection. Adrenaline, phlorhizin, and diabetic puncture have no influence on the liver diastases.

H. V. ATKINSON

The relationships between radium and life. ADOLF KORLSCH. *Schweiz. Chem.-Ztg.* 1920, 635-9.—A popular review treating the various causes of atm. radioactivity and the effect of Ra rays on bacteria and molds, the eggs, spermatozoa and embryos of various animals, the seeds of plants and certain tissues of mature organisms. An unsuccessful attempt at the spontaneous generation of life with the aid of Ra rays is mentioned.

NORRIS F. HALL

The occurrence of bromine as a normal constituent of animal tissues. A. DAMIENS. *Bull. sci. pharmacol.* 27, 609-26(1920).—A historical and critical review is given of the various methods of detg. Br in animal tissues, the conclusion of which is that the observations of Labat (C. A. 7, 1902) are incontestable from the qual. point of view but quantitatively are inexact because on the one hand the H₂O extrn. of the Mg compd. used in the combustion is incomplete, and on the other hand the method of sepn. of the Br is imperfect. Cf. C. A. 15, 219.

F. S. HAMMETT

Zymase and alcoholic fermentation. J. GIAJA. *J. physiol. path. gén.* 18, 1094-1114(1920).—G. detd. the degree of fermentation produced in his expts. by measuring the CO₂ evolved. He found that the addition of toluene to living yeast cut down the fermentation power some 95%, while the activity of zymase as such is hardly affected. When live yeast is put with sucrose the max. activity is obtained in 30 to 40 min. When toluene is added to the yeast suspension at the moment of mixing with the fermentable sugar there also occurs a rise in activity during the first 30 min. But if toluene is added to the yeast before suspension the rise in activity is inhibited. When toluene is added to yeast in full fermentation activity this drops exactly to the value of the resting yeast. On the other hand the inverting capacity of the yeast is almost unaffected by the addition of toluene to the fermenting mixt. These observations lead G. to consider that there is yet no proof that the fermenting power of living yeast can be apportioned integrally to zymase, and that only a very feeble part of this activity can be indisputably attributed to activity of enzyme. Cf. C. A. 14, 3004.

F. S. HAMMETT

Studies on hemocyanin. CH. DUBRÉ. *J. physiol. path. gén.* 18, 1081-93(1920); cf. C. A. 14, 1139, 2211.—From a study of the absorption spectra of oxyhemocyanin in the ultraviolet range D. concludes that no matter what the zoological source of the material may be 2 absorption bands are common to all the oxyhemocyanins examd.

F. S. HAMMETT

The changes of creatine and creatinine. AMANDUS HAHN AND GEORG BARKAN. *Z. Biol.* 72, 25-36(1920).—The authors studied the reciprocal changes of creatine and creatinine in alk. and acid solns. The creatine used was prepd. by sepn. from muscle ext. The creatinine was purchased. All detns. were made colorimetrically and creatinine solns. were used as standards. The expts. showed that the reaction of the change from creatine to creatinine and *vice versa* is an incomplete reaction of the first

order and has a well defined point of equilibrium. In acid soln. creatine goes completely over into creatinine with the formation of a soln. of creatinine cations.

F. S. HAMMETT

Origin of the melanin from pyrrole. P. RONDONI. Firenze. *Sperimentale* 74, 157-70(1920).—Preliminary expts. with rabbit skin exts. (saline) showed that in the case of black rabbits, incubation with a weak pyrrole (A) soln. caused slight browning, which was intensified to a black in the presence of FeSO_4 , showing no differences from the skin exts. of white or gray rabbits in the presence of this salt. It thus appears that the ability to oxidize A *in vitro* is greater in the case of pigment-forming skins than in those incapable of color production. While A has some action in increasing the production of pigment in the skin of rabbits *in vivo*, its action is not as great as that of α -pyrrole carboxylic acid, whose increased action is ascribed to its far slower elimination.

M. HEIDELBERGER

Enzyme activity as influenced by hydrogen-ion concentration with special reference to the Koji enzymes. ANON. *Tokyo Igakukai Zasshi* 32, No. 23, 1-30(1919); *Jap. Med. Literature* 5, 44(1920).—The optimum H-ion concn. for the enzymes of Koji (*Aspergillus oryzae*) was found to be: Protease (acting on coagulated egg white) 4.7, peptase (acting on Witte peptone) 4.7, amylase 4.85, maltase 4.1, invertase 5.0.

JOSEPH S. HEPBURN

Heat production during the action of enzymes. B. INOUE. *Tokyo Igakukai Zasshi* 32, No. 21, 1-34(1918); *Jap. Med. Literature* 5, 44(1920).—During proteolysis, on the av., 0.17 small cal. of heat is produced for each mg. of amino N. The amt. of heat is proportional to the increase in the number of mols. in the digestion mixt. A mixt. of 2 proteases produces from 1.4 to 1.6 times the sums of the amts. of heat and of proteolysis (measured by the formol titration) produced when each enzyme acts separately. During the hydrolysis of urea by urease 97.2 small cal. are produced for each g. of substrate decomposed. During the enzymic hydrolysis of 1 g. of maltose, 4.66 cal. are produced, and during the alcoholic fermentation of 1 g. of glucose 134.9 cal.

JOSEPH S. HEPBURN

Report on teaching of biochemistry. OTTO FOLIN, P. A. SHAFFER AND A. P. MATHEWS. *Proc. 30th Annual Meeting Assoc. Am. Med. Colleges* 1920, 107-14.—Discussion of the course in biological chemistry in schools of medicine; special attention is paid to the subject matter of such a course.

JOSEPH S. HEPBURN

Some influences of French science on medicine. GRAHAM LUSK. *J. Am. Med. Assoc.* 76, 1-8(1921).—In this "Pasteur Lecture" Lusk gives a most interesting account of the wonderful work of Lavoisier, and brief sketches of the work of a few French chemists of the 19th century.

L. W. RIGGS

Considerations concerning the nature and origin of physiological gradients. C. M. CHILD. Univ. Chicago. *Biol. Bull. Marine Biol. Lab.* 39, 147-83(1920).—"This paper is a survey of the evidence bearing upon certain aspects of the problem of integration or pattern organisms. The organism represents a definite pattern or integration of some kind. The pattern of the organism is of a higher order of magnitude than protoplasmic pattern since it involves masses of protoplasm or even cells each of which may possess the entire protoplasmic or cell pattern. Protoplasm apart from environment does not appear to possess any inherent mechanism for originating such pattern. While specific differences appear in the development and differentiation of pattern in each organism, in its more general features such as polarity and symmetry, this pattern appears to be largely independent of specific differences in protoplasmic constitution. This fact suggests that it represents primarily a non-specific or quant. condition or relation in a specific protoplasm. Many different lines of evidence which are briefly reviewed indicate, first, that the simplest form of axiate pattern is primarily a gradient in physiological condition, involving the fundamental metabolic reactions as well as

various other factors, and second, that such gradients arise in the final analysis from differential exposure to external factors which affect the rate of protoplasmic activity. The primary physiol. relations established in this way are those of excitation and transmission but from the first moment of differentiation chem. or transportive correlation becomes possible and plays an increasingly important role in the progress of development." Cf. *C. A.* 14, 430. L. W. RIGGS

Pyrrole and melanuria. III. PIETRO SACCARDI. Univ. Camerino. *Gazz. chim. ital.* 50, II, 118-28(1920); cf. *C. A.* 14, 551, 2033, 3411.—Data from the literature are reviewed in support of the statement that black pigments in animals are due to the transformation of tyrosine. S. did a variety of expts. from which he concludes that tyrosine is not capable of giving rise to melanin. It is quite resistant to org. and inorg. oxidizing agents. Adrenaline is more sensitive and with Cl-water gave a brown ppt. that looked like melanin. More material is needed to finish the expts. Injection expts. with pyrrole in man show that his power of intraorg. oxidation lies between that of rabbits and guinea pigs and that of dogs, in which it is rapidly destroyed. These animals all react to pyrrole as though the organism were accustomed to it. The organism can also reduce melanin to melanogen. The formation of melanoid compds. by boiling albumin and carbohydrates with concd. mineral acids was confirmed for egg white but not with glucose. This product does not give the characteristic reaction of Thormählen. E. J. WITZEMANN

Unsaturated bile acids (BOEDECKER) 10.

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

Contents of the stomach: its study and interpretation. ELBRIDGE J. BEST. *Am. J. Med. Sci.* 160, 880-97(1920).—A detailed account is given of the technic of the use of the Rehfuess tube and test meals. H. V. ATRINSON

Demonstration of cow milk in human milk. C. KAPPELLER AND A. GOTTFRIED. *Münch. med. Wochschr.* 67, 813-4(1920).—The color changes in the Unikoff reaction, the refraction of the acetic acid serum and the difference in the acid coagulation of the caseinogen are used to show the addition of 20% or more cow milk to human milk. At that it is necessary to compare the results with milk from the same woman whose milk is suspected of addition. S. AMBERG

Estimation of tryptophan in proteins. PIERRE THOMAS. *Ann. inst. Pasteur* 34, 701-8(1920).—The tryptophan content of proteins has been measured by direct isolation and weighing (Hopkins and Cole, *J. Physiol.* 27, 418 (1901)), by digestion and titration with Br water, a change from red-violet to yellow indicating the complete monobromination of the tryptophan (Levene and Rouiller, *C. A.* 1, 1019), by use of the glyoxylic acid color reaction of Hopkins and Cole, comparison being made colorimetrically with a standard containing pure tryptophan (Fasal, *Biochem. Z.* 44, 392(1912)), and by a similar method using *p*-dimethylaminobenzaldehyde (Herzfeld, *C. A.* 8, 941). T. finds the Herzfeld method reliable if certain precautions are followed, the chief of which is to assure complete soln. of the protein used. T.'s modification of the method is as follows: Dissolve 0.4 g. of the very finely powdered product, so fine that it will pass through stretched silk, in 200 cc. of 0.5% Na₂CO₃ containing 0.1 g. of pancreatin. Add 5 cc. CHCl₃ and 5 cc. C₆H₅CH₃ as preservatives and incubate the mixt. 5-7 days or to the max. intensity of the Br reaction. Remove 50 cc., add 10 cc. of a reagent containing 20 g. *p*-dimethylaminobenzaldehyde, 500 cc. concd. HCl, and 500 cc. water, and dil. the mixt. to 100 cc. with concd. HCl. Allow to stand in the light 48-60 hrs., and compare the color developed with a standard of pure tryptophan treated in an identical manner. Correction is made for the tryptophan content of the pancreatin. By this method the tryptophan content of casein

was found to be 1.7-1.8%, a result agreeing closely with the values obtained by Hopkins and Cole on isolation and weighing.

E. R. LONG

Note on the indole test in tryptophan solution. CHR. BARTHEL. Agr. Expt. Station, Stockholm. *J. Bact.* 6, 85-8(1921).—The tryptophan soln. of Zipfel is equally satisfactory without lactate, but under all conditions it must be neutralized.

JOHN T. MYERS

A composite reagent for the determination of sodium chloride in urine. H. V. ATKINSON. Univ. Illinois. *J. Lab. Clin. Med.* 6, 180(1920).—In order to avoid sep. measurement of water, HNO_3 , and satd. ferric ammonium alum soln. in the chloride test A. used the following soln.: AgNO_3 6.87 g., ferric ammonium alum 75 g., concd. HNO_3 150 cc., water to 1000 cc. Shake 90 cc. of this reagent in a cylinder with 10 cc. urine. Let settle, pipet off 50 cc. of the clear supernatant fluid and titrate the excess AgNO_3 with standard NH_4SCN soln., 1 cc. of which equals 4.5 cc. of the above soln.

E. R. LONG

Indices of enzymes of the blood. Estimation of catalase, peroxidase and esterase in one drop of blood. A. BACH AND MME. SOPHIE ZOUBKOFF. *Compt. rend.* 171, 967-9(1920).—In a 75 cc. conical flask are placed 7 cc. H_2O , 1 cc. blood dild. with pure perfectly neutral 1% H_2O_2 , the mixt. agitated and placed in a thermostat at 37° for 30 min. A control test is made at the same time upon 1 cc. of the blood soln. previously heated to boiling. After 30 min. in the thermostat, 3 cc. $\text{N H}_2\text{SO}_4$ are added to each flask, and the undecompd. H_2O_2 is titrated with 0.1 N permanganate. The difference in the amt. of permanganate used indicates the H_2O_2 decompd. by 1 cu. mm. of blood and furnishes a measure of the catalase. In a narrow test-tube are placed 7 cc. H_2O , 1 cc. of 0.1% pure guaiacol, 1 cc. dild. blood and 1 cc. 1% H_2O_2 . The mixt. gradually assumes a reddish brown color which attains a max. in 15 min. A control test upon 1 cc. dild. blood previously heated to boiling remains colorless, the peroxidase reaction being much more evident than that of hemoglobin. The amt. of guaiacol oxidized under these conditions is estd. colorimetrically for a measure of the peroxidase. Two-tenths g. of K sulfoguaicolate in 7 cc. H_2O are placed in a narrow test-tube with 1 cc. 1% H_2O_2 , 1 cc. dild. soln. peroxidase, 1 cc. blood dild. 1 to 1000 and allowed to stand 30 min. In proportion that the ester is divided by the action of the esterase, the guaiacol liberated is oxidized by the peroxidase and H_2O_2 . A control test is made upon 1 cc. of blood previously boiled. The quant. figures for esterase are obtained colorimetrically. The results of 40 tests, using 1 cc. blood, were: *Catalase*, max. 18.78, min. 17.17, av. 17.8 mg. H_2O_2 decompd.; *peroxidase*, max. 0.153, min. 0.096, av. 0.121 mg. guaiacol oxidized; *esterase*, max. 0.147, min. 0.108, av. 0.131 mg. of guaiacol set free and oxidized.

L. W. RIGGS

Comparative determination of total nitrogen in urine by the Dumas and Kjeldahl methods. W. MESTREZAT AND MISS MARTHE-PAUL JANET. *Compt. rend.* 171, 1019-21(1920).—Ten specimens of urine collected from 3 persons for 4 or 5 days following the taking of 30 g. Na_2SO_4 gave an av. of 3.4% more N by the Dumas than by the Kjeldahl method, the extremes being 0.3 and 9.7%.

L. W. RIGGS

Estimation of degradation of protein materials in the blood serum. A. BACH AND B. SBARSKY. *Compt. rend.* 171, 1175-7(1920).—Previous work by Bach proved that the reduction of nitrates and of coloring matter in animal tissues is detd. by the combined action of an enzyme and coenzyme, the latter originating in the products of protein degradation which are changed to aldehydes by the decompn. of amino acids. Fresh milk contains the enzyme without the coenzyme, a fact which permits its use in estg. the degradation products of proteins. Expts. with 7 horses, 3 immunized to diphtheria, 2 to dysentery and 2 to scarlatina, were made as follows: In a test-tube was placed 1 cc. serum, 0.2 g. NaNO_3 and 2 cc. fresh milk, the tube placed in a thermostat at 60° for 30 min., then 3 cc. of 5% lead subacetate were added, the ppt. was filtered out

and 3 cc. of the clear filtrate tested for nitrites by the method of Hosvay-Lunge. Controls were made on the fresh milk previously heated to boiling and on fresh milk with 1 cc. H_2O in place of the serum. With fresh milk from a healthy cow the controls showed no nitrite. The serum of each animal was tested before injection. Generally the max. of nitrite appeared within 2 days after injection and rapidly diminished after 3 days. The amt. of N_2O_5 found was used as a measure of the amt. of degradation products.

L. W. RIGGS

Method of microscopic radiopenetration; a means of analysis and experimental cytology. SERGE TCHAHOTINES. *Compt. rend.* 171, 1237-40(1920).—The details are given for arranging prisms, microscope and other optical devices for obtaining an extremely fine ultraviolet beam ($280\ \mu\mu$) and directing it upon the different parts of a cell. The arrangement appears to form an important addition to the methods for the study of cytologic problems.

L. W. RIGGS

Clinical method for the determination of blood sugar in minute quantities. ISRAEL S. KLEINER. *J. Am. Med. Assoc.* 76, 172-3(1921).—This method is based on Benedict's most recent technic (cf. *C. A.* 12, 1304), modified for use with a new microcolorimeter which is illustrated and described in detail. The method is simple, quick, accurate and requires only 0.2 cc. of blood.

L. W. RIGGS

A photoelectric colorimeter. F. WILDERMUTH. *Arch. ges. Physiol.* 183, 91-108 (1920).—Quant. differentiation of minute variations in the concn. of hemoglobin is possible with the colorimeter described. Details of construction and operation are given.

G. H. SMITH

Standardization of laboratory methods (WADSWORTH) 7. Estimation of histidine (THRUN, TROWBRIDGE) 7.

C—BACTERIOLOGY

A. K. BALLS

Preparation of a simplified culture medium for field workers. DOROTHY NORRIS. Central Research Inst., Kasauli. *Indian J. Med. Research* 7, 704-9(1920).—A substrate containing 10% of caseinogen in a 0.8% soln. of washing soda was digested with 0.5% pancreatic ext. at 37° for 24 hrs. The digest was filtered through muslin, neutralized and concd. on the water bath, a paste of the consistency and color of Liebig's ext. of meat being thus obtained. This paste will keep for at least 6 months and does not require the addition either of peptone or meat extract but may be made up into solid nutritive medium merely by the addition of agar and normal saline or tap water. It is especially good for *B. typhosus*. The name "trypsinoids" is given to the powder.

H. V. ATKINSON

Pellicle formation in broth culture by *Bacillus cholerae*. K. R. K. IVENGAR. Central Research Inst., Kasauli. *Indian J. Med. Research* 7, 701-3(1920).—Pellicle formation by the cholera vibrio and probably indole formation are dependent on the alkalinity of the medium used.

H. V. ATKINSON

Standardization of disinfectants with special reference to those used in the chemical sterilization of water. S. R. CHRISTOPHERS, K. R. K. IVENGAR AND W. F. HARVEY. Central Research Inst., Kasauli. *Indian J. Med. Research* 7, 803-9(1920).—The suspension of organisms used in testing disinfectants should be one of naked organisms in a menstruum containing no org. matter; special coeff. should be devised for the evaluation of the effect of org. matter. Iodine is a better indicator for the testing of water-sterilizing substances than phenol. Coeffs. of stability, price, portability and poisonous character are required to complete the description of a disinfectant.

H. V. A.

The toxicity towards *Staphylococcus* of dilute phenol solutions containing sodium benzoate. KENNETH E. BURGESS. Univ. Toronto. *J. Phys. Chem.* 24, 738-40(1920).—B. detd. the rate at which staphylococci are killed by PhOH solns. containing varying

amts. of PhCOONa , following the method of Lemon (*C. A.* 15, 120). Low concns. of the salt have hardly any effect on the toxicity of PhOH and the efficiency of the former as a life preserver in the dil. solns. is in accord with the explanation of Laird (*J. Phys. Chem.* 24, 664), which refers them to plasmolysis. A. L. BARKER

The action of methylene blue and certain other dyes on living and dead yeast. CHAS. G. FRASER. Univ. Toronto. *J. Phys. Chem.* 24, 741-8 (1920).—The purpose of this investigation was to find a method for detg. simply and rapidly the no. of yeast cells alive after immersion for a measured time in a poisonous liquid. The following dyes were used: Grüber's methylene blue, fuchsin, Congo red, erythrosin, safranin, Merck's methylene blue, gentian violet, methyl green, Kahlbaum's methylene blue 6B extra. Aq. solns. (0.5 g. per 100 cc.) of the dyes were added to suspensions of living yeast and yeast killed by boiling and by the action of PhOH . Erythrosin and methylene blue give the best results: in both cases living cells were not stained at all in a few minutes, whereas dead cells were all stained within 1 min. The effect of the dyes in dil. soln. on the reproduction of yeast in culture media was also studied; reproduction in a malt ext. soln. took place in every case. With higher concns. of dye, when all cells were stained, no reproduction occurred. In the case of methyl green, cells may lose their power of reproduction without being stained. A. L. BARKER

The gas production of Streptococcus kefir. JAMES M. SHERMAN. U. S. Dept. of Agr. *J. Bact.*, 6, 127, (1921).—The conclusion is drawn that the CO_2 produced by organisms of the *Streptococcus kefir* type, when grown in ordinary lactose broths, is derived from the carbohydrate portion of the media. With reference to the CO_2 produced in the ripening of Cheddar cheese, after the original lactose content of the cheese is exhausted, it would not be safe to draw conclusions. From expts. with this streptococcus in various sugar-free media, and in media containing a variety of organic acids, it would appear doubtful whether it can be held responsible for the normal CO_2 production of Cheddar cheese. JOHN T. MYERS

Bacteria concerned in the ripening of corn silage. P. G. HEINEMANN AND CHARLES R. HIXON. *J. Bact.* 6, 45-51 (1921).—The authors offer the following as a tentative hypothesis. The fermentation consists of three phases brought about by three groups of bacteria. The initial phase is accompanied by acid and gas formation, is of short duration, and is caused by the colon-aerogenes group of bacteria. The second phase is accompanied by a moderate acid formation, and is carried on by streptococci. The third phase is the result of the activity of lactobacilli and may be divided into minor phases due to different strains of lactobacilli. This hypothesis does not interfere with the assumption that the first stage is a respiratory process. There is no evidence of an alc. or acetic acid fermentation. JOHN T. MYERS

Powdered litmus milk. A product of constant quality and color which can be made in any laboratory. HERBERT W. HAMILTON. Mass. Inst. Tech. *J. Bact.* 6, 43-4 (1921).—The dye should be a blue azolitmin as free as possible from the red dye. It may be prepared by the following method. Ext. litmus cubes with boiling distd. water, decant, evap. to a thin paste, add an excess of glacial CH_3COOH , evap. to dryness, add a quantity of 95% alc., filter, wash the residue with alc., dissolve it in distd. water, add a little NaOH if necessary, and evap. to dryness. Add one part of this dye to 52.7 parts of dried skim milk powder. Dissolve the resulting powder in distd. water in the ratio of one part powder to 9.5 parts of water. JOHN T. MYERS

The nature of toxin. The antigens of *Corynebacterium diphtheriae* and *Bacillus megatherium* and their relation to toxin. C. C. WARDEN, J. T. CONNELL AND L. E. HOLLY. Univ. Mich. *J. Bact.* 6, 103-26 (1921).—*Corynebacterium diphtheriae* and *B. megatherium* possess characteristic fat complexes which are, under proper colloidal conditions, the true antigens of both these organisms. Artificial fat complexes have replaced the antigens of the germ bodies in the various immune reactions. The lysins

and toxins of the *C. diphtheriae* and *B. megatherium* are the same substances, being the specific fat complexes of the respective organisms, existing in definite and particular colloidal states. Aside from colloidal or emulsifying activity cellular protein appears to have no place in the immune reactions studied.

JOHN T. MYERS

Chemical criteria of anaerobiosis with special reference to methylene blue. IVAN C. HALL. Univ. Chicago. *J. Bact.* 6, 1-42(1920).—H. reviews the literature on chem. criteria of anaerobiosis. The decolorization of methylene blue is studied in detail and is shown to depend on the action of org. substances, especially carbohydrates, with alkali. There is a definite correspondence between Fehling's test and the decolorization of methylene blue. There is a direct relationship between the amt. of dye decolorized by heating and the amts. of alkali and glucose, and an inverse relation between the last two factors in the test, so that an increase in one permits a decrease in the other for the same result. CO_2 as well as O is a factor in the recolorization of methylene blue. Paraffin wax is greatly superior to liquid paraffin in protecting decolorized solns. of the dye from recolorization and vaseline is much more efficient than solid paraffin, as shown by tests with *B. welchii*, *B. letani*, *B. botulinus* and other obligate anaerobes. Adsorption plays a large part in the decolorization of methylene blue by plant and animal tissues. Extn. of fragments of potato with 0.1 N HCl, neutral water, or 0.1 N NaOH yielded a substance, starch, which was capable of reducing the dye. Animal tissue treated in the same way did not yield a reducing substance, but if kept in the soln. overnight in the ice-chest before boiling a reducing substance was extd. The exact O tension to which the reduction of methylene blue corresponds has not been detd. nor has it been ascertained whether decolorization occurs at a definite H-ion concn. irrespective of the sugar content of the soln.

JOHN T. MYERS

A further investigation into the principles underlying the Gram stain, with special reference to the bacterial cell membrane. T. H. C. BENIANS. *J. Path. Bact.* 23, 401-12(1920).—The factors underlying Gram's stain are inherent in the physical structure of the bacterial cell, and are not conferred on it by the application of the mordant, although they are brought out more easily, as regards both positive and negative characters, in that way. There is nothing in the nature of a chem. fixation of the dye to the bacterial substance in those organisms that retains the stain when the cell is intact, and the amorphous bacterial substance of either positive or negative organisms shows no marked difference as regards the extn. of the dyes by alc. The effect of the mordant is to dissociate the dye from its adsorption compd. with the tissues, forming with it a large molecular body, which in alc. soln. does not easily pass out of the bacterial body. The capacity for retaining the dye in Gram-positive cells is chiefly dependent on the structure and integrity of the limiting cell membrane, so that the large dye-iodine mol. does not readily pass through it in alc. soln. It is probable that the imbibition of water from weak alc. solns. alters the permeability of the membrane of the gram-positive cell so that the dye can escape. There are two types of Gram-negative bacteria as regards their cell membrane; those that allow the attachment and probable permeation of methyl violet and Victoria blue, and those in which these dyes are only peripherally adsorbed. The first type is represented by the gonococcus, and the second by the coliform bacilli.

JOHN T. MYERS

Influence of luminous radiations upon a fixation of nitrogen. E. KAYSER. *Compt. rend.* 171, 900-71(1920).—Expts. were made with *Azobacter agile*, a bacterium characterized by great motility, the formation of pigment and fluorescence. The inoculated culture media in conical glasses were inclosed by glasses colored red, yellow, green, blue, violet, black and white and placed along side of a window where the sun penetrated but slightly, from July 1 to Oct. 20, at lab. temp. Cultures contained 3.04% mannitol with salts and a min. amt. of CaCO_3 . As time passed the media assumed different colors

under the differently colored glass inclosures. Mannitol completely disappeared from the cultures under the yellow, black and green shades. In the others were crystals of mannitol. The total N ranged from 11.04 mg. under the violet glass to 18.06 under the yellow, the increasing order being violet, white, green, black, red, blue, yellow. For each g. of mannitol decompd. 8.59 mg. of N were formed under the violet, 5.94 under the yellow and 4.22 under black. With glucose in place of mannitol the most N was found under the green and the next largest amt. under the yellow inclosure. In the glucose series the fixation of N per g. of glucose decompd. was quite uniform, the extremes being 6.36 mg. under the violet and 7.76 under the blue.

L. W. RIGGS

In vivo as *in vitro* bacteria pass through the wall of the filter. J. Y. HEYMANS. *Compt. rend.* 171, 971-3 (1920); cf. C. A. 6, 3441.—In reed sacs, duly tested, and containing 0.05 g. dry potato powder, was introduced 1 to 2 mm. of a wire laden with anthrax spores. The extremities of the sac were sealed, covered with collodion, placed in a gelatin capsule and introduced into the peritoneal cavity of the rabbit. At the end of 2 to 3 days each rabbit so treated died from anthrax infection. In a second series of expts. the prepd. reed sacs were plunged in simple collodion, removed and allowed to evaporate and again coated with collodion 5, 10, or 20 times, placed in gelatin capsules and administered to rabbits as before. Death follows in every case but was retarded 5 to 15 days. In a third series 30 coatings of an elastic ricinic collodion were employed covering the sac with a layer 1 mm. thick. These were administered to rabbits and death by anthrax infection was delayed but followed in every case. These results confirm the hypothesis of ultramicroscopic bacterial diapedesis.

L. W. RIGGS

Factors influencing anaerobiosis, with special reference to the use of fresh tissue. FREDERICK L. GAYES AND PETER K. OLITSKY. Rockefeller Inst. Med. Research. *J. Exp. Med.* 33, 51-68 (1921).—Liquid paraffin oil, used extensively as a seal for anaerobic cultures and in gas analysis, has very little value in inhibiting the access of O. Solid vaseline forms an effective O-resisting seal. Fresh kidney tissue is an active reducing agent, and quickly decolorizes methylene blue in its vicinity. The reducing effect is relative to the amt. used. As a reducing agent, at least 0.6 g. per tube is required for the establishment of an adequate O-free zone. Culture media may be classified as reducing or non-reducing. Those containing dextrose or peptone in a faintly alkaline soln. belong to the former class. Ascitic fluid and dil. serum belong to the latter class. Semisolid media effectively inhibit the penetration of O to the depths of the tube, but they likewise inhibit the diffusion of reducing substances and presumably of nutrient substances from imbedded kidney tissue. The length of the column of medium is of minor importance under a vaseline seal. Suggestions are made for the establishment of strictly anaerobic conditions in the culture tube.

C. J. WEST

Development of cultures. W. O. FROTHING. *Cream and Milk Plant Mo.* 9, No. 12, 48-56 (1920).—Taking up the various growth factors conceded to influence the development of bacterial cultures F. seeks to correlate these with the ripening of certain dairy products with *Streptococcus lacticus*. He contends that the titrable acidity of lactic acid cultures may be expressed in terms of the H-ion concn. if use is made of the expression $H^+ = \sqrt{K C}$, and shows its derivation. The growth curve is expressed in terms of lactic acid. The strength of the bacterial culture consists in its possessing a short lag phase and the ability to go through a logarithmic growth phase; also it should have a short generation time in the logarithmic growth phase. A temp. of 20° is most favorable to the maintenance of pure cultures of the above organisms. From 12 to 14 hrs. is the best ripening time to use in making cultures or fermented dairy products such as com. buttermilk. The effect of age of culture, etc., upon the lag phase is discussed.

H. F. ZOLLER

D—BOTANY

CARL L. ALSBERG

The biologic significance of the tannic substances. Variations of tannin content in the bark of the chestnut tree according to months and the seasons. A. DE DOMINICIS with the collaboration of R. SPATARO. *Stas. sper. agrar. ital.* 52, 305-31 (1919). —The tannin was extd. by repeated treatment with boiling H₂O and the detns. were made according to the Löwenthal-Schröder method with the following results:

% TANNIN ON DRY BASIS.

	Plants 2 yrs. old.			Plants 5 yrs. old.					Plants 20 yrs. old.		
	Trunk Base	Trunk.		Branches.			Leaves and buds		Trunk.		Branches 7 yrs. old
		Base	Middle	4 yr. old	3 yr. old	2 yr. old			Base	Middle	
Nov.....	12.90	10.80	9.27	7.70	8.34	10.15
Dec.....	12.64	10.96	10.62	8.66	8.66	8.78
Feb.....	10.48	13.06	11.08	10.56	9.87	9.74
Mar.....	10.11	10.65	9.69	9.10	9.42	9.28
Apr.....	10.11	11.19	8.34	9.88	12.03	12.57	8.24	8.19
May.....	6.63	7.17	8.12	4.95	5.65	12.26	5.82	3.40	4.10
July.....	6.60	7.00	6.80	6.83	4.25	4.20	5.80	3.72	4.05
Sept....	11.57	14.08	8.22	8.08	7.29	6.75	7.17	5.14

Ten drops of 10% tannin soln. added to 20 cc. 0.1% albumin soln. caused coagulation, merely opalescence in the presence of 6 drops of citric acid and had no effect in the presence of 6 drops of AcOH or tartaric acid (all 10%). The tannin tends to diminish during the period of max. physiol. activity. By origin, constitution and phys. and chem. properties tannins should be considered as glucosidic in nature, esterification compds. of aromatic oxy-acids such as gallic and protocatechuic acids and a sugar, most commonly glucose. Tannin is a very strong protoplasmic poison, coagulating albumin. It appears in the germination of seeds, which are initially free from it, and hence cannot be considered as a reserve material for either the sugar contained or for those compds. which, accumulating in the free state, would be harmful. Tannic substances may be considered as secondary products of exchange of materials but in this sense the esterification of the phenolcarboxylic acids forming their nucleus cannot be attributed to the same reason as the formation of other glucosides, namely the neutralization of the toxicity of products resulting from vegetable metabolism, for gallotannic acid is more toxic than gallic. Wood shows a much higher coeff. of absorption for tannin than for gallic acid, yet the more easy elimination of the tannic substances in the glucosidic state by the absorptive action of the cellulose of the wood cannot be the only reason for their formation. The principal reason is their more easy oxidizability in comparison with the phenolcarboxylic acids from which they are derived. The tannin disappears by complete oxidation in fleshy fruits when the coagulating power of the tannin itself is no longer neutralized by the free org. acids which disappear with maturation. In other organs, however, an equil. is established between the tannin which is formed in or brought to the organ and that which is destroyed by combustion. In the bark, directly exposed to the oxygen-containing atm. and to variations in the external agents, this equil. is subject to displacements, the most significant of which is caused by the increased oxidation brought about by rise in temp. which reaches its max. during the hottest months of the summer. Tannic substances, therefore, in the glucosidic state, represent refuse material which the plant can easily destroy by the vital process of combustion.

ALBERT R. MARR

The distribution of enzymes and proteins in the endosperm of the wheat berry. F. J. MARTIN. *Wellcome Tropical Research Lab. J. Soc. Chem. Ind.* 39, 327-8T,

348T(1920).—Enzymic activity, as shown by the evolution of CO_2 on fermentation, increases from the interior to the exterior of the endosperm, as does also the gluten content. The quality of the gluten deteriorates in the same direction. The tests were made on Barusso Plate wheat.

T. G. PHILLIPS

The excretion of toxins from the roots of plants. J. N. MUKERJI. *Agr. J. India* 15, 502-7(1920).—Knop nutrient solns. having the following compn.: $\text{Ca}(\text{NO}_3)_2$ 4 g., $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 1 g., KNO_3 1 g., KCl 0.5 g., FeCl_3 trace in 7 l. H_2O , was used in this study, the total salt concn. being 0.11%. Plants were grown in separate portions of the soln. with the idea of studying plant root excretion. The growth of the second set of plants proved superior to growth in fresh soln. The high concn. of salts in the 1st growth soln. is held to be the cause of poor growth. The conclusions of Flether (*Men. Dept. Agr. India, Bot. Ser. II*, No. 3) that plants excrete toxic substances are held to have been reached because of the high concn. of the soln. he used rather than because of plant excretions.

J. J. SKINNER

E—NUTRITION

PHILIP B. HAWK

NORMAL

Curves of sugar and urea after standard protein meals. AAGE TH. B. JACOBSEN AND HAROLD EDWARDS. Allen Clinic, New York City. *Am. J. Med. Sci.* 159, 833-43 (1920).—After a standard meal of 50 g. protein there is generally a rising curve of urea in the blood, which, as a rule, is higher in patients with severe diabetes or nephritis than in normal persons. The blood-urea level is not a reliable index of nitrogen retention. In some instances, for example in diabetics, it may possibly bear some relation to the rate of protein katabolism. On the whole, it seems to be governed by so many factors of the previous diet, fluid retention and unknown metabolic conditions that by itself it forms an uncertain basis for conclusions. The plasma sugar of normal persons is not appreciably altered by this quantity of protein. The substances in nephritic blood, which react like sugar to the Benedict test, are increased after a protein meal. A typical curve of hyperglucemia follows the ingestion of protein in suitably severe cases of diabetes. This is likely to be missed if active symptoms of glucosuria or hyperglucemia are present, as the effect of 50 g. protein could scarcely be expected to be noticeable amid such a surplus of sugar. Rarely also the rise may be slight in extreme exhaustion. Under the conditions of strict diet treatment this reaction to a standard protein meal may be used as a measure of the severity of diabetes and a guide both to the protein allowance and the total ration, and it has lately been used for these purposes in this clinic.

H. V. ATKINSON

Preservation of the antiscorbutic properties of cabbage by drying. AXEL HOLST AND THEODORE FROLICH. Univ. Christiania, Norway. *J. Trop. Med. Hyg.* 23, 261-3 (1920).—(1) Thin slices of cabbage which are dried for 1 week in an incubator at 37° and thereupon at the same temp. by means of P_2O_5 show very pronounced antiscorbutic properties when kept at 37° for 18 to 26 months in vacuum bottles. (2) The same cabbage lost almost all of these properties when not treated with P_2O_5 but kept for 18 months at 37° in closed vessels with CaCl_2 . (3) If treated as under (2) the cabbage keeps its properties much better at 4° to 12° . (4) The results are better than mentioned under (2), but not so good as under (3), when the cabbage is kept at 4° in closed vessels without any drying agent.

H. V. ATKINSON

Intermediary metabolism and the enzymes concerned therein. TORSTEN THUNBERG. *Skand. Arch. Physiol.* 40, 1-91(1920).—T. studied the reactions of intermediary metabolism by observing the decolorization of methylene blue under various conditions. When striated muscle of a freshly killed frog is extd. sufficiently long with H_2O it loses its power, which it previously had, of decolorizing methylene blue in O_2 -free soln. This power, however, is restored when certain substances are added to

the muscle-methylene blue system, although these compds. themselves have no direct decolorizing effect. An analysis of a succinic acid-muscle-methylene blue system showed that the decolorization process consists in the transference of 2 H atoms from the succinic acid to the methylene blue through the mediation of an enzyme, a so-called "hydrogen-transportase," the reaction yielding on the one hand an acid of less H content, and on the other the leuco compd. of methylene blue. Other compds. exhibit this property of restoring the activity to the muscle tissue. Among those studied, lactic, fumaric, both α - and β -hydroxybutyric, malic, *l*-tartaric, *l*- α -hydroxyglutaric, citric and glutamic acids all gave positive reactivating effects. As a result of these observations T. is of the opinion that the simple materials such as glucose, fat, and amino acids which are brought to the cells as nourishment, pass through a whole series of intermediate stages before final disposal. An early step in this chain of reactions is a "dehydrogenation" or indirect oxidation, combined in certain cases with hydrolysis, or CO_2 splitting. A whole series of dehydrogenating or hydrogen-transferring enzymes takes part in the accomplishment of these reactions. These enzymes are generally specific for the different intermediary compds. The H that is removed from these compds. can either unite with O_2 to form H_2O , or can be used to hydrate other compds. On this basis all foodstuffs are H-donors: more fundamentally H is the common fuel of the cells.

F. S. HAMMETT

The fate of the acetone bodies in intermediary metabolism and on sugar formation from fat. H. CHR. GHELMUYDEN. *Skand. Arch. Physiol.* 40, 211-25(1920).—When oil is added to the diet of phlorhizinized rabbits the glucosuria already existing is increased. A slight increase in N excretion is also obtained. Hence the possibility exists that the increased sugar output is due to an increased protein destruction. When phlorhizinized dogs are given injections of butyric, acetic or caproic acid in the form of the Na salts the sugar output is increased over an extended period.

F. S. HAMMETT

Neuro-metabolism. I. The neuro-metabolism of the medulla oblongata. THEODOR BRUGSCH, KURT DRESSEL AND F. H. LEWY. *Z. exp. Path. Ther.* 21, 358-79 (1920).—The object of the study was to det. the influence of the various parts of the nervous system on metabolism. Rabbits were used as the exptl. animals. When N and blood-sugar equil. had been established a lesion was made in the medulla oblongata by means of a fine needle. Different parts of the medulla were destroyed in different animals and the effects on the blood and urine detd. At autopsy the exact location of disturbance was detd. and correlated with the metabolic alterations. It was found when the so-called vagal centers, even of one side only, had been affected that hyperglucemia and glucosuria had followed. This then leads to the conclusion that these nuclei are to be considered as sugar centers. Retrograde degenerations extending from the dorsal vagal nucleus involved the periventricular nucleus, close to the 3rd ventricle, and at times the habenular ganglion of the same side. The ganglia-cells of the formatio reticularis on the median side of the restiform body proximal to the parotid secretory center are centers for NaCl and H_2O metabolism. For within an hour and a half after disturbance of this locality the NaCl of the blood increased markedly. No centers affecting the metabolism of uric acid and the purines could be found.

F. S. HAMMETT

Some effects of water-soluble vitamins upon nutrition. WALTER G. KARR. Yale Univ. *J. Biol. Chem.* 44, 255-76(1920); cf. *C. A.* 15, 382.—Data concerning the role of vitamins in nutrition have been obtained for the most part from expts. on small animals such as birds, rats, mice and guinea pigs. In the expts. conducted by K. the relation of the H_2O -sol. B vitamin to the nutrition of the dog has been studied. The standard diets contained either wheat gluten or com. casein as the source of protein and the remaining caloric requirements were supplied by sucrose and lard. The diets

were practically free from fat-sol. and anti-scurvy vitamins but the animals exhibited no symptoms which might be taken as indicating specifically a lack of either of these vitamins. Some relation was found to exist between the desire to partake of food and the amt. of H_2O -sol. vitamin ingested; most of the dogs ultimately refused to eat any of the mixts. unless vitamin-containing food was given. The desire to eat could be quickly restored by the ingestion of a substance such as brewery yeast, bakers' yeast, tomatoes and milk which contains H_2O -sol. vitamin. The vitamin prepn. was fed apart from the food so that the palatability of the ration was not affected. Feeding fat-sol. vitamin had no such effect in influencing the appetite. 1.5 g. of commercially dried brewery yeast, 3 g. of com. moist bakers' yeast, 200 cc. of canned tomatoes, or 150 cc. of milk were in all cases sufficient to bring the food intake back to normal. Drying at 100° did not affect the efficacy of these vitamin preps. but autoclaving at 120° for 3-4 hrs. led to some destruction. Mammalian polyneuritis developed in several animals which continued to eat the ration despite the absence of H_2O -sol. vitamin. They could not walk, finally could not stand and generally lay with their legs sprawled out at the side; severe tetanic convulsions occurred especially when handled or set down quickly on the floor; the head was in motion and there were often tremors and twitchings of the muscles. These symptoms could be relieved and practically eliminated within a few hrs. by administering brewery yeast or tomatoes, substances rich in H_2O -sol. vitamin.

A. P. LOTHROP

Metabolism studies with diets deficient in water-soluble (B) vitamin. WALTER G. KARR. *Yale Univ. J. Biol. Chem.* 44, 277-82(1920).—"It has been suggested that vitamins may exert their unique function in intermediary metabolism or in the glandular secretory processes connected with digestion in the alimentary tract. With this possibility in mind studies of N metabolism were made with animals on similar diets, resp. rich in or devoid of H_2O -sol. B vitamin. The general plan was to compare the metabolism of an animal recently placed on a vitamin-free diet with its metabolism at a later period on the same diet; also to compare the metabolism on a vitamin-free diet with periods in which a supply of H_2O -sol. B had been added, and to control the possible supplementing action of the protein of the crude vitamin-yielding substance by a further period in which a corresponding amt. of purer protein was added." Four female dogs were employed and were given diets in which com. casein or wheat gluten furnished the protein, and lard and sucrose the remaining calorific requirements. Brewery yeast was used to supply the H_2O -sol. vitamin. "The data are very consistent in showing that the N utilization in the digestive tract was unaffected by the absence of H_2O -sol. vitamin. From this the conclusion may be drawn that the secretions of the glands intimately associated with digestion and absorption were not materially affected by the lack of the accessory food factors. Small quantities of a good protein in the form of casein or yeast exerted a remarkable effect on the N balance of an animal which was consuming proteins of wheat gluten which are known not to be so 'complete.' In view of the small portions (3-6% of the total protein) sufficient to produce this result, the quantities of amino acids involved in the deficiencies must have been small at most."

A. P. LOTHROP

A deficiency in heat-treated milks. AMY L. DANIELS and ROSMARY LOUGHLIN. *Univ. Iowa. J. Biol. Chem.* 44, 381-97(1920); cf. *C. A.* 10, 788.—It has previously been shown by Daniels and Stuessy that rats fed milk boiled 1, 10 and 45 mins. resp., grow slowly, fail to attain the wt. for normal animals and never reproduce. In these expts. the milk was brought slowly to the boiling point, requiring about 35 min. and then boiled for the time mentioned. The expts. have been repeated using milk heated quickly to the boiling point and boiled 1 min., with milk heated slowly to the boiling temp., with milk pasteurized by the "hold" method, and with com. canned milk, both sweetened (condensed) and unsweetened (evapd.). Rats fed quickly heated milk grew

normally and to all appearances were perfectly nourished animals. "The results of all the expts. on the long heat-treated milks point to the same conclusion; namely, that, in the process of heating, the Ca salts are rendered more or less insol., depending upon the length of time the milk is heated. In this insol. form they may be lost, owing to the fact that some of the pptd. material adheres to the container, as in the case of long pasteurized or slowly heated milk, while some, for example in evapd. milk separates out on standing. When especial care was taken to include the insol. material by colloidal suspension, results comparable to those on raw and quickly boiled milk were obtained. No data were obtained indicating that either the fat-sol. or the H_2O -sol. vitamins in milk is affected by heat treatment, nor is casein apparently affected. Rats fed superheated milk with $Ca_3(PO_4)_2$ properly incorporated made normal gains. The inferior growth of rats on the long heat-treated and superheated milk appears to be due wholly to the readjustments of the inorg. complexes. The application of these findings to infant nutrition is now under investigation." $Ca_3(PO_4)_2$ was effective only when it was incorporated in a corn-starch paste in which it is held in suspension by the colloidal soln. The growth of the rats fed on undild. condensed milk was practically normal. This milk was of a thick, semisolid consistency and any insol. Ca salts formed during the condensing process were, therefore, held in suspension and the animals were able to obtain all the Ca phosphates present.

A. P. LOTHROP

Experimental studies on growth. XVI. The influence of brain tissue, freed from cholesterol, upon the growth of the white mouse. T. BRAILSFORD ROBERTSON AND L. A. RAY. Univs. Adelaide and Toronto. *J. Biol. Chem.* 44, 439-53(1920); cf. *C. A.* 14, 2363.—"The nervous system can be shown (a) by its importance for the regeneration of lost parts; (b) by the significance of the ratio of brain wt. to body wt. in detg. the longevity of animals, and (c) by the dystrophy following upon nerve section, to exert a stimulating influence upon the growth of parenchymatous tissues. The stimulation of growth by nervous tissues may conceivably be due either to the nervous impulses conducted by them or to a substance officiating as a growth hormone which is conducted to the tissues wholly or in part through nerve fibers. In conformity with the latter view it is shown that substances which stimulate the growth of parenchyma in mice (tethelin and cholesterol) so modify the time relationships of growth as to bring about an approximation of the growth curve for mice towards the form of the growth curve for human beings, in which the ratio of brain wt. to body wt. is much higher than it is in mice. Cholesterol has previously been shown to modify the growth of mice in the manner indicated. Its effect, even in high dosage, is, however, much less than the effect of a high ratio of brain wt. to body wt. If the nervous system affects growth through the agency of a sp. catalyzer or hormone, therefore, this substance must be more potent than cholesterol. Brain tissue from which cholesterol has been extd. by cold acetone, administered by mouth in dosage of 36 mg. (containing 4 mg. of cerebrosides), is without effect upon the growth of mice. It is inferred that if the nervous tissues do contain a potent catalyzer of growth other than cholesterol it is also sol. in cold acetone and is removed from the brain in the process of extg. the cholesterol."

A. P. LOTHROP

The antiscorbutic content of certain body tissues of the rat. The persistence of the antiscorbutic substance in the liver of the rat after long intervals on a scorbutic diet. HELEN T. PARSONS. Johns Hopkins Univ. *J. Biol. Chem.* 44, 587-602(1920).—The problem of whether the antiscorbutic substance is essential in the normal metabolism of the rat has been approached from the standpoint of detg. the antiscorbutic content of rat tissues when a typical scurvy-producing diet was fed and when the diet contained an abundant amt. of antiscorbutic substance. The exptl. rats were fed for 213-247 days on a soy bean ration which has been found satisfactory in producing scurvy in guinea pigs. The control animals were fed a stock ration with 5 cc. of orange juice per rat per day, together with an aq. ext. of orange peel added to the drinking

water. Scurvy was induced in guinea pigs by a soy bean ration and they were then fed varying amts. of liver obtained from rats, chloroformed the day the tissues were used for feeding. "The rapid disappearance of the symptoms of severe scurvy substantiated by postmortem findings and correlated with the resumption of eating and a rapid gain in wt., during the 15 days (or less) when the guinea pigs were fed the livers of rats which had for a long time consumed a typical scurvy diet, leaves no doubt that this tissue with this history is rich in the antiscorbutic factor. It was, in fact, effective in relieving the symptoms of scurvy at such a low level of intake (5 g. during a period of 11 days) that, without the use of larger numbers of animals, it could not be said that the livers of the control set of rats which had consumed orange juice were richer in this factor. This demonstration of such considerable amts. of the antiscorbutic factor in the livers of these rats disposes fairly definitely of the hypothesis that the rat may not require antiscorbutic substance for its normal metabolism. It seems entirely improbable that the presence of this factor in the bodies of these animals should be accidental, especially since the amts. in the bodies of the two sets of rats approximate each other so closely. A synthesis of this factor is indicated, both by these results, and by the excellent growth and reproduction obtained in rats by feeding a ration containing wheat, casein, dextrin, salt mixt., and butter fat, in which no constituent has been shown to allay scurvy symptoms in the guinea pig. Closely allied to this hypothesis of a synthesis is the possibility that the rat can utilize some slightly different inactive forms of the antiscorbutic substance into which the active form might theoretically pass on ageing, drying, etc., and from which it might be rapidly changed in such physiological processes as the sprouting of seeds. An alternative explanation is that the rat has a very definite food requirement for the antiscorbutic factor but that this is quantitatively very small in comparison with the requirement of the guinea pig. Some constituent of the diet might presumably carry sufficient quantity for the requirement of the rat, but escape detection in the light of the much larger requirement of the guinea pig. But if this explanation is accepted it is surprising to find such an abundance of the factor in the bodies of the rats fed on the scorbutic soy bean diet. It would be logical to assume that an extremely small requirement for the food factor would not necessitate the presence of a relatively large supply of that factor in the body of the animal. It is conceivable that the rat has acquired not only a lowered requirement but also a phenomenal capacity to store the antiscorbutic substance through a biological adaptation to a food supply which over long periods of time is very deficient in this substance." A. P. L.

The antiscorbutic requirements of the prairie dog. E. V. MCCOLLUM AND HELEN T. PARSONS. Johns Hopkins Univ. *J. Biol. Chem.* 44, 603-7(1920).—The western prairie dog, *Cynomys ludovicianus*, a rodent, behaves like the rat rather than the guinea pig insofar as its antiscorbutic requirement is concerned. It is capable of growing for several months and remaining free from any symptoms of scurvy on a diet which entirely fails to protect the guinea pig. Growth occurred during a period of 6 months on a scorbutic soy bean flour diet which is equiv. to 9-12 times the interval that is necessary for the development of scurvy in the guinea pig subsisting on the same diet.

A. P. LOTHROP

A critic of experiments with diets free from fat-soluble vitamins. THOMAS B. OSBORNE AND LARAYETTE B. MENDEL. Conn. Agr. Expt. Station and Yale Univ. *J. Biol. Chem.* 45, 277-88(1921).—Very divergent results have been obtained by various investigators on feeding young rats diets in which lard was the sole fat. In some cases growth at quite normal rate occurred for 60-80 days; in others little, if any growth resulted under apparently similar conditions while Daniels and Loughlin (*C. A.* 14, 3102) obtained growth, reproduction and rearing of young with rats on diets in which the only apparent source of fat-sol. vitamins was lard or cottonseed oil. These conflicting results raise the question of the complete freedom from fat-sol. vitamins of the foods

used in the different expts. and the whole problem has been subjected to further critical investigation. The diet consisted of casein or edestin, com. corn starch and dried brewery-yeast, all of which had been purified by boiling 3 times with abs. alc. under a reflux condenser for 1 hr. Such extn. of yeast does not diminish its potency as a source of H_2O -sol. vitamine. To these substances were added a salt mixt. and either com. or alc.-extd. lard. When rats were fed this ration there was a reduction of the period of undiminished growth but there was for some time a not negligible increment of wt. After a decline had begun, prompt recovery resulted from the addition of butter fat. "It has been alleged that the ability of animals to grow for some time in the supposed absence of fat-sol. vitamine is due to 'exceptional vitality' of the individuals or to reserve stores of the vitamine in the body. Unless we are to accept some indefinite explanation of this sort, it seems necessary to conclude in the light of our experience, that removal of the fat-sol. vitamine from even purified proteins and carbohydrates is accomplished with far greater difficulty than has been hitherto suspected. An entirely convincing crucial expt., in which nutritive failure immediately ensues upon the administration of diets fully adequate in every respect except for the presence of fat-sol. vitamine, remains to be made. It is significant that older rats thrive for a longer time than do the younger ones on the same diets nearly if not entirely free from the fat-sol. vitamine. This is in contrast with the well established fact that at all periods the lack of H_2O -sol. vitamine is speedily manifested." There was no essential difference in the results obtained with alc.-extd. lard, com. lard and lard rendered at comparatively low temps. in the lab.

A. P. LOTHROP

Comparative metabolism of proteins of unlike composition. WALTER G. KARR. Yale Univ. *J. Biol. Chem.* 45, 289-95(1921).—While it is well known that the proportions of the end-products of N metabolism in the urine may be varied by the nature of the diet, it has not been definitely ascertained whether this partition of N can be altered by the type of distribution of N in the protein intake, *i. e.*, whether amide and amino N have the same fate in metabolism. Female dogs were fed diets differing only with respect to the character of the protein. The proteins used were casein containing about 12.7% of N and yielding 10.5% of its N as NH_3 when hydrolyzed for 2 hrs. with 20% HCl and wheat gluten having 12-14% of N and yielding about 22% of it as NH_3 under the same conditions. "As far as is indicated by the urinary nitrogenous end-products, the metabolism of the two proteins, widely different in their chem. make-up, is essentially the same. Despite the great diversity in amide N in the proteins compared, the relative excretion of urinary NH_3 was approx. the same. The creatinine output was evidently entirely of endogenous origin and the creatine found seemed independent of the nature of the protein. In metabolism expts. with comparable quantities of yeast as the sole source of protein, the partition of urinary N compared favorably with what was observed after feeding the other two proteins. The utilization of the yeast protein was about 80%."

A. P. LOTHROP

ABNORMAL

Observations on cases of rickets in an out-patient department. HELEN M. M. MACKAY. Queen's Hosp., London. *Brit. Med. J.* 1920, II, 929-32.—A clinical investigation of 51 children (46 under 3 yrs.). The results showed the impossibility of obtaining sufficiently accurate data from outpatient work to draw definite conclusions, but are in accordance with the generally accepted view that rickets is a dietetic disease, commonly developing in children receiving insufficient fat and too much carbohydrate, especially when bottle-fed.

A. T. CAMERON

Ornithuric acid formation in starving hens. T. SUGA. *Kyoto Igaku Zasshi* 15, No. 6, 225-9(1919); *Jap. Med. Literature* 5, 46(1920).—Starving hens (unlike well fed birds) are unable to synthesize hippuric acid from benzoic acid and glycocoll; they con-

jugate ingested benzoic acid with ornithine into ornithuric acid, and excrete the latter compd.

JOSEPH S. HEPBURN

Xerophthalmia in fowls fed on polished rice and its clinical importance. L. E. GUERRERO AND I. CONCEPCION. *Philippine J. Sci.* 17, 99-103(1920).—In the biological assay of ext. of *tikitiki* with chickens as the exptl. animals, blindness associated with cachexia has occurred in both the controls and the test fowls. The 5 controls were fed a ration of polished rice exclusively; they developed polyneuritis; 1 bird became blind but lived for more than 100 days. Of the 30 test fowls, which were on a diet of polished rice and also received 5 cc. of *tikitiki* ext. daily, 5 developed polyneuritis, and 7 died after developing xerophthalmia which appeared as early as the 7th day and as late as the 79th day of the expt. The deductions are drawn (I) that polished rice lacks not only the antipolyneuritic vitamine (water-sol. B) but also the anti-xerophthalmic vitamine (fat-sol. A) which also governs growth, and (II) that *tikitiki* ext. contains water-sol. B, but not fat-sol. A. Unpolished rice probably contains fat-sol. A. The classification of xerophthalmia as a deficiency disease is also discussed. J. S. H.

Experimental infantile scurvy. M. SUGAWA. *Tokyo Igakukai Zasshi* 22, No. 20, 1-36(1918); *Jap. Med. Literature*, 5, 39(1920).—Guinea pigs, which were fed a proprietary infant food for 2 to 3 weeks, developed the lesions which are typical of human infantile scurvy.

JOSEPH S. HEPBURN

Studies on experimental rickets. I. The production of rachitis and similar diseases in the rat by different diets. E. V. MCCOLLUM, NINA SIMMONDS, H. T. PARSONS, P. G. SHIPLEY AND E. A. PARK. Johns Hopkins Univ. *J. Biol. Chem.* 45, 333-41(1921).—Eleven diets are described out of more than 300 modifications which have been found to produce rachitic and related pathological conditions in the skeleton of the rat. The diets were deficient in one or more of the following respects: Fat-sol. A, Ca, excess of potential acidity, protein. "Each of these diets, when fed supplemented with purified food additions to make good the deficiencies, is capable of inducing approx. normal nutrition and normal skeletal growth. With these factors corrected there is in no instance any evidence from the general appearance of the animals of the deformities so characteristic of those restricted to the deficient formulas. The present discussion is of necessity a preliminary communication, and we are not willing to hazard any statements in regard to the factors operating to produce rickets in the child or the exptl. animal. It might seem that the cause of these diseases lies in a deficiency of fat-sol. A or Ca in the food, or a disturbance in the metabolism of these factors. Many years' experience with feeding expts., however, have demonstrated how dangerous it is to draw conclusions from apparently obvious data. Any suggestions regarding the absence of a sp. antirachitic substance or deficiency of either fat-sol. A and Ca as the primary agent in the production of rickets would be ill considered and might be far from the truth. At present it is only possible to say that the etiological factor is to be found in an improper dietary regimen. The large variety of dietary formulas the administration of which results in rickets and kindred affection gives abundant evidence of the complex nature of the causes operating in the production of the disease. We shall attempt the presentation of their analysis in later papers." II. The effect of cod liver oil administered to rats with experimental rickets. P. G. SHIPLEY, E. A. PARK, E. V. MCCOLLUM, NINA SIMMONDS, AND H. T. PARSONS. *Ibid* 343-8.—The cartilages and metaphyses of the bones of rats can be freed from Ca deposits by subsistence on a diet deficient in fat-sol. A for 40 days or longer. The addition of cod liver oil to the food for a period of from 2 to 7 days is followed by a deposition of Ca salts between the cells of the proliferative zone of cartilage. "The results of this series of preliminary expts. afford ocular and conclusive evidence of the sp. beneficial effect of cod liver oil on rats suffering with exptl. rachitis, in that some substance or substances in the oil cause Ca to be deposited in the same fashion in which deposition occurs in spontaneous healing

of rachitis in man. Moreover, they prepare the way for the elaboration of a new test, which it is hoped may eventually prove even to be roughly quant., for the detn. of the Ca-depositing potentiality of any substance in terms of cod liver oil units. It is especially interesting to note that Ca was deposited in the cartilages following the initiation of the cod liver oil treatment in spite of the fact that in some cases the Ca intake was far below normal. In view of the fact that in human cases of rickets the blood Ca is maintained throughout the disease at approx. the normal level it is interesting to speculate concerning the source from which the Ca deposited in the proliferative cartilage is derived. Expts. are now under way with a view to perfecting the biological test reported and to detg. the Ca-depositing power of certain other possible therapeutic agents."

A. P. LOTHROP

Experimental studies in diabetes. II. The internal pancreatic function in relation to body mass and metabolism. FREDERICK M. ALLEN. Rockefeller Inst. *Am. J. Med. Sci.* 160, 781-801 (1920); cf. *C. A.* 14, 2380.—Dogs show an increased tendency to glucosuria from glucose given by stomach or subcutaneously when as little as $\frac{1}{4}$ or $\frac{1}{8}$ of the pancreas is removed. Apparently, therefore, the pancreas has little if any "margin of safety" from the standpoint of strictly normal metabolism, and there may be frequent occasions when its full endocrine function is needed for the purpose of fully normal assimilation. Quantities of sugar which exceed the normal assimilation may possibly be conceived as overtaxing the normal pancreatic function. The internal secretory potency of different parts of the pancreas is equal as far as such tests can be; but the influence of a given mass of tissue increases as the total mass of remaining tissue decreases. The "margin of safety" of the pancreas with regard to diabetes is large, amounting in the dog to at least seven-eighths of the gland. The point at which diabetes begins is sharp and definite, according to three criteria: (a) An animal may be brought so close to the verge of diabetes that it is brought on by the removal of as little as 0.1 g. additional tissue. (b) At this point a new histological phenomenon begins, namely, the degeneration of the islands which is the basis of the characteristic aggravation of diabetes on excessive diets, while such excesses are harmless in any states of lowered tolerance short of diabetes. (c) The lowering of tolerance in any stage short of diabetes is only apparent, representing only a slight delay of assimilation while the actual capacity is unlimited, and the maintenance of continuous glucosuria through any long period of weeks or months is absolutely impossible by any quantity of sugar or any other food; but in diabetes the limit of assimilation is real and glucosuria progressively increases to the point of total excretion of the quantity administered. The curve of lowering of tolerance, with removal of successive portions of pancreas, is therefore approx. hyperbolic in form. Starting as a variable which descends by successive slight degrees below the level of normal tolerance, it turns at the vertex into a variable which approaches total diabetes as its limit. Certain conceptions concerning the quant. relations of the pancreatic hormone may be deduced as follows. It stands in some quant. relation with the amt. of carbohydrate metabolized, because a deficiency is revealed by moderate glucose dosage when only $\frac{1}{4}$ of the pancreas is removed, and because of the above-mentioned proof that in diabetes the islands can be driven to destructive overfunction by carbohydrate excess and spared by regulation of diet. A more important quant. relation is the minimum requirement of the body cells to prevent diabetes. When this minimum quantity of the hormone is present the organism retains its power to metabolize almost the whole of any glucose dosage that can be absorbed from the stomach or subcutaneous tissue, no matter how large or how long continued. When this minimum is reduced by only a trifle the phenomena of diabetes begin. With mild diabetes this deficit may be guarded against by restriction of carbohydrate.

With more severe diabetes the total diet and body weight must be reduced. With still more severe diabetes the supply of hormone is inadequate for even the lowest metabolism and glucosuria is therefore uncontrollable even by fasting. As an example it may be assumed that a dog becomes diabetic with removal of between $\frac{1}{3}$ and $\frac{1}{10}$ of the pancreas, and in this condition requires maximal starch and sugar feeding to maintain glucosuria. Hopeless diabetes, uncontrollable by fasting, results (barring hypertrophy) when the remnant is about $\frac{1}{20}$ of the pancreas. The absolute difference between these fractions may be, for a fair-sized dog, perhaps 2 g. of pancreas tissue. Accordingly the differences between the demands of the highest possible carbohydrate metabolism and the demands of the lowest possible general metabolism amounts in such an animal to no more than the possible output of 2 g. of pancreatic tissue, only a small fraction of which consists of islands. Such a calcn. is of interest in animals when quant. estns. can be made with approx. accuracy by operations. There is evidently a fallacy in the application to human patients, for it is impossible that the destruction of islands in human diabetes should always fall within the narrow limits mentioned. As a matter of fact, diabetes uncontrollable by fasting is very common in experimental animals and very rare in human cases. A possible explanation may be that one prominent feature of human cases is a functional defect which interferes with the internal secretory activity of the islands and at the same time renders them specially susceptible to damage from functional over-stimulation. Such an explanation is supported by observations in other directions. One of these is the abundance of normal appearing islands in some clinical cases necessitating the assumption of a functional impairment. Another is the wide variation in the susceptibility of different human patients (especially the old and young) to degeneration of islands and corresponding decline of tolerance from dietary excess. At the same time it seems evident that a relatively small mass of normal island tissue can prevent diabetes, and the conclusion is, therefore, suggested that any positive means of augmenting the endocrine pancreatic function even by a little would give therapeutic results far surpassing those of the negative plan of sparing the function of diet.

H. V. ATKINSON

F—PHYSIOLOGY

ANDREW HUNTER

Significance of small amounts of sugar in the urine. LUDWIG KAST, EMMA L. WARDELL AND VICTOR C. MYERS. New York Postgraduate Med. School. *Am. J. Med. Sci.* 160, 877-83(1920).—Qual. sugar observations on hourly specimens of urine show that the results obtained from the usual qual. tests made upon specimens of urine taken at random, or even in the morning before breakfast, are misleading as regards the carbohydrate tolerance of the patient.

H. V. ATKINSON

Variation in the chromaffin substance of the suprarenals in diabetes of central origin. IJURO FUJII. Tohoku Univ. Sendai. *Tohoku J. Exp. Med.* 1, 38-72(1920).—The chromaffin substance of the suprarenals changed after the production of diabetes of central origin but not until after onset of glucosuria. Evidence is given to show that in rabbits the splanchnic nerve on each side innervates the epinephrine secretion only on the same side.

H. V. ATKINSON

Changes of the constituents of the urine after section of the renal nerve. RYOICHI YOSHIMURA. Tohoku Univ. Sendai. *Tohoku J. Exp. Med.* 1, 113-9(1920).—Expts. on rabbits lead Y. to conclude that the increase of the urine after section of the renal nerve is due to the acceleration of the renal circulation caused by the loss of vaso-constrictor impulse of the renal nerve. The change of the constituents of the urine is the outcome accompanying the increase of the urinary vol.

H. V. ATKINSON

Salt glucosuria. KOICHI NAITO. Tohoku Univ. *Tohoku J. Exp. Med.* 1, 131-52(1920).—The injection into rabbits of 10% NH_4Cl , NaCl and HgSO_4 , after having

cut both splanchnic nerves, disproves the hypothesis that salt glucosuria is due to the increased permeability of the kidneys. Maintenance of the body temp. does not prevent salt hyperglucemia but does check salt glucosuria to a large extent. Inhalation of air rich in O does not change the hyperglucemia or the drop in body temp. after subcutaneous injections of salts but does reduce the glucosuria. H. V. ATKINSON

Action of serum from nephritis on sympathetic nerves. TOYOJIRO KATO AND MASAO WATANABE. Tohoku Univ. Sendai. *Tohoku J. Exp. Med.* 1, 167-86(1920).—Expts. by the frog method of Trendelenburg show that the vasoconstricting principle in the serum in cases of chronic nephritis is different from that present in normal serum and is not epinephrine. It is destroyed at 56°, by drying and upon standing but not by cold. It is insol. in alc. and ether, is removed from serum with albumin and does not dialyze through a membrane. **Epinephrine mydriasis with chronic nephritis.** *Ibid* 187-291.—The mydriasis due to epinephrine instilled into the eyes of chronic nephritics parallels the blood pressure. It seems to be due to the active principle mentioned above. It is generally negative in cases of acute nephritis.

H. V. ATKINSON

The internal secretion of the pancreas. T. KUMAGAR AND S. OSATO. Tohoku Univ. Sendai. *Tohoku J. Exp. Med.* 1, 153-66(1920).—The internal secretion of the pancreas passes into the blood by way of the lymphatics. Exptl. pancreas diabetes in dogs is reduced by lymph obtained from the thoracic duct after the injection of pilocarpine.

H. V. ATKINSON

Physiological action of typhoid toxin. JUNKICHI SOGEN. Univ. Sendai. *Tohoku J. Exp. Med.* 1, 211-86(1920).—An extensive series of clinical and lab. expts. attempting to explain the relative slowness of the pulse with the high fever of typhoid. **Influence of pneumococcus toxin on the circulation.** *Ibid* 287-338.—After extensive studies, S. concludes that the disturbance in the circulation caused by this toxin is due to a primary injury to the heart. **Influence of bacterial toxins on the intestines.** *Ibid* 339-51.—The peristaltic movement of the surviving intestine is not affected by cholera or pneumococcus toxins. Dysentery toxin poisons Auerbach's plexus; strepto-toxin poisons the intestinal muscle. Extensive bibliographies are appended. H. V. A.

Relation of lack of chlorides in the animal body to hydrochloric acid of the gastric juice. MAKI TAKAYA. Tohoku Univ. *Tohoku J. Exp. Med.* 1, 354-66(1920).—T., experimenting with a Pavlov fistula dog, finds that even when the lack of chlorides in the body has reached a high degree, it affects the Cl content and acidity of the gastric juices very little.

H. V. ATKINSON

Effects of the emotions on gastric secretion and motility in the human being. T. I. BENNETT AND J. F. VENABLES. Guy's Hospital. *Brit. Med. J.* 1920, II, 862-3. —Using Rehffuss fractional method of gastric analysis on normal human subjects, comparisons were made with a test meal normally digested, and digested under hypnosis, when various suggestions were made. Nausea inhibits the usual sharp rise in acidity. Suggestion of hunger produces no effect unless made at a stage where distinct acidity is developing, when marked acidity greater than normal is produced, with a striking increased rapidity of emptying. This is considered to indicate a fundamental law, that in a stomach secreting HCl, any increase in the rate of emptying will by itself det. an increase in acidity of content. Anxiety produced an increased initial acidity (? hyperadrenalism producing quickening of peristalsis) followed by marked inhibition of production and delay in the emptying rate.

A. T. CAMERON

Gastric digestion. T. I. BENNETT AND J. A. RYLE. *Brit. Med. J.* 1920, II, 503. —Rehffuss' conclusions are confirmed, that estn. of gastric acidity at any single moment after a test meal is often grossly fallacious. "Hyperchlorhydria" and "hypochlorhydria" do not signify pathol. entities; both occur frequently in healthy subjects.

A. T. CAMERON

Effects of thirst on the weights of the various organs and systems of adult albino rats. T. KUDO. Univ. Minnesota. *Am. J. Anat.* 28, 399-430(1921).—Two series of expts. were carried out. In one, dry food only, or dry food with rapidly diminishing amts. of milk, was fed (acute thirst); in the second, dry food was fed with slowly diminishing amts. of milk (chronic thirst). In the acute thirst series the av. gross body wt. fell 36% in a few days, in the second series, over 50% in a much longer period. The loss in wt. of the different organs was similar, and similar also to that in a rat kept in complete inanition for 11 days, and to the wt. changes obtained by other observers for inanition with water. It is uncertain whether this similarity is because the primary effect of thirst is the same as that of other forms of inanition or whether the thirst effects are largely obscured by the accompanying inanition due to inadequate food intake.

A. T. CAMERON

Study of cerebral metabolism by the method of partial circulation. H. RENAULD-CAPART. *Arch. intern. physiol.* 25, 235-89, 411-45(1920).—The principle of partial circulation is based on the localization of the circulation by suitable operative procedures to the organ, the functions of which it is desired to study, conserving the heart as motor power, and the lungs as oxygenators; if occasion demands the kidneys and the adrenals can also be left in the circuit as mechanisms for the removal of waste and the regulation of arterial pressure. Preliminary studies are reported in which the influence of variations in the blood pressure on the functions of the nerve centers has been investigated. When the blood pressure was very low, owing to exclusion of the adrenals, and the activity of the nerve centers was lowered the injection of adrenaline did not restore their activity though it did raise the blood pressure. But since in some cases the central functions still persist even with the low pressure it is evident that a mesencephalic circulation is still in force; however, the irritability of the central nervous system is markedly diminished. Apparently then the disappearance of the activity of the cerebral centers is not due to variations in circulation of the blood. Other expts. cited also indicate that this loss of activity is not due to a cooling of the cerebral centers, to a deficiency in pulmonary circulation or oxygenation of the blood. On the other hand when an animal has become unconscious, and gives no evidence of central activity (excepting, of course, cardiac and respiratory), if the blood is allowed to re-circulate through the abdominal organs there occurs a resumption of activity by these centers. The conclusion is that the abdominal blood is essential for the life of the encephalic nerve centers. The second part of this interesting study is concerned with the role played by the liver in the activity of the neural centers. The detailed expts. show that when the liver is *not* cut out of the circulation the centers continue to function. This is not due to a detoxicating action of the liver because the blood of a dog in which the liver is out of the circulation does not contain toxic substances capable of arresting the functioning of the cerebral centers. Accordingly, R. attributes this sustenance of cerebral function by the liver inclusion in the circulation to the production of an internal secretion by this organ, which is indispensable to cerebral metabolism. That is to say, there exists an evident functional relation between hepatic function and the activity of the cerebral centers. The cerebral activity in its totality is immediately dependent upon a special hepatic function, a function of internal secretion, which up to the present has been ignored.

F. S. HAMMETT

The chemical composition of the thymus and the weight relations between this organ and the thyroid. EDGAR ZUNZ. *Arch. intern. physiol.* 25, 459-72(1920).—Observations on the thymus gland obtained from individuals from 14 to 44 years of age showed that it is exceptional to find a thymic atrophy in an adult man in full health dying by accident. The wt. of the gland in man from 19 to 34 years is around

15 g. but it may weigh more than 30 g. In spite of the large individual variations the % of Et_2O extractives tends to increase with age, though it is relatively const. in the healthy adult. The lipid P content of the thymus is relatively const. and is not very great. Extensive tables are given of the ash, N, P_2O_5 , dry matter, lipoid P, and Et_2O extractives of the individual glands studied. No relation exists between the dry wt., N, P, and ash and the age of the subject, according to the wt. of the fresh thymus. The wt. of the fresh thymus is always more than that of the thyroid when this gland weighs less than 19 g.

F. S. HAMMETT

The energy output during walking on flat or rising ground. H. MAONE. *J. physiol. path. gén.* 18, 1154-75(1920).—When walking on level ground the energy output as measured by the O_2 consumption increases with the amplitude and rate of the steps. This output involved in carrying out the movements accompanying an increased stride, and of strides of accustomed length is at a minimum at a rate of 100 half steps a min. A man naturally chooses the rate and length of his stride that yields the most economical utilization of energy. The minimum output in relation to the space traversed is at a rate of approx. 63 m. per min. When walking is done on rising or falling ground the supplementary output due to the work of ascent or descent is not added to the fixed output of level ground walking. The new conditions of body equilibrium adjustment allow for a substantial reduction from the otherwise total output.

F. S. HAMMETT

The excretion of urine by herbivora. J. CHAUSSIN. *J. physiol. path. gén.* 18, 1123-53(1920).—C. detd. the concn. of urea, Cl, sol. alkali of the ash expressed as K_2CO_3 , the Δ , and the ext. at 105° of the urine of rabbits and other herbivora. He found that the ratio $(\delta u + \delta c)/\Delta$ varied between 0.20 and 0.40 in these types of animals while the same ratio in man is around 0.75. The alkali carbonates are present in the urine of herbivora in significant amts., largely as K_2CO_3 . The chlorides can be neglected in a primary approximation of the compensatory phenomenon between the alkalinity and the urea. This compensation simulates that existing between urea and chlorides in man. When NaCl was added to the diet of the herbivora there becomes evident an always const. antagonism between the alkali of the ash and the urinary Cl. In fact, the compensatory mechanism plays between the 3 substances: urea, chlorides and alk. ash, but is more striking and more lasting between the 2 latter.

F. S. HAMMETT

The variability in the action of hypophyseal extracts. JACQUES PARISOT AND PIERRE MATHIEU. *J. physiol. path. gén.* 18, 1182-93(1920).—As has been known for a long time hypophyseal exts. have two opposite actions on both the heart and the vascular system. The dynamogenic action, in the sense of a stimulation, results from weak doses; the anti-dynamic actions result from the strong doses. A weak dose is defined as one which is physiol. active at the moment when it is not directly determinable in the circulation medium. The threshold of these two actions can vary for the same individual, for each individual and for each tissue in an absolute fashion and because of local circulatory changes, and in such a way that local toxic effects can be produced by doses non-toxic to the organism. As far as the living organism is concerned, however, the dynamogenic effects are practically the only ones that are possible or realized under physiol. or therapeutic conditions.

F. S. HAMMETT

Contributions to the localization of "sweet smell." E. ROCKN. *Stand. Arch. Physiol.* 40, 129-44(1920).—The results of this investigation show that there is no marked alteration in the min. perceptibility of the sensation of sweetness in the smell of CHCl_3 , CHBr_3 , $\text{C}_6\text{H}_5\text{CHO}$, and octyl alc. after energetic gargling of the mouth and throat with 0.5% soln. of gymnema together with flushing the floor of the nasal cavity and the nasal surface of the velum palatinum with the same soln. On the other hand,

after the same treatment the min. perceptibility of the sweet component of anethole was increased from 1.3×10^{-3} g. mol. per l. to 14×10^{-3} g. mol. per l. Only in the case of anethole could a sensation of taste be shown to exist as an essential ingredient of the "sweet smell."

F. S. HAMMETT

Static muscular work. J. LINDHARD. *Skand. Arch. Physiol.* **40**, 145-95, 196-210 (1920).—Studies of the respiratory exchange during static work showed that the O_2 consumption is increased but slightly and that when the period of effort is over the metabolism rises markedly. In one case where the work lasted 0.9 min. and where the total metabolic increase on account of the work was about 1123 cc. O_2 , but 168 cc. of this fell in the work period itself, while 955 cc. were used in the first 6 min. after cessation of effort. On the basis of these studies L. concludes that the static contraction of muscle causes a mechanical obstruction to the flow of blood in the activated tissue; that the static muscular work is, therefore, largely anaerobic; and that the rapid onset of fatigue is due to an accumulation of lactic acid in the working muscle. An extension of the studies seemed to indicate that the respiratory quotient both during and after the work period varied regularly with the type of respiration. The quotient increased during the work in every case; but when the respiration during the effort was abdominal, the quotient was still more increased in the after-period, with the opposite effect occurring when respiration was of the thoracic type during the work period.

F. S. HAMMETT

Secretive activity of the anterior lobe of the hypophysis in pregnancy. ATTILIO GENTILI. Univ. Sassari. *Sperimentale* **74**, 286-91 (1920).—In the anterior lobe of the hypophysis of pregnant cows there occurs, with the advance of gestation, an increase in the lipoids and a progressive accumulation of "colloid substance." Toward the end of pregnancy all the cells show signs of active secretion. The lipid was isolated by Binaghi's method (*Ann. ostetricia e ginecologia*, 1916); it belonged to the phosphatide group.

M. HEIDELBERGER

Theories on coagulation of the blood. JULES BORDET. Inst. Pasteur, Brussels. *Ann. inst. Pasteur* **34**, 561-95 (1920).—A review.

E. R. LONG

An attempt toward the determination of the total alkaline reserve of the body. W. PRENTICE, H. O. LUND AND H. G. HARBO. Univ. Minn. *J. Biol. Chem.* **44**, 211-3 (1920).—The object of the expts. was to det. the max. amt. of acid that could be injected into the blood stream of the dog without more than neutralizing the alk. reserve of the blood plasma, a procedure which would be expected to draw upon the alk. reserve of the whole body. Warm 0.1 N HCl in 1% NaCl was passed into the external jugular vein at a uniform rate, the flow of acid being continued until signs of coma appeared and the heart action became very weak. The vol. of the body is approx. 20 times that of the blood plasma, and if the alk. reserve of the whole body is the same as that of the blood plasma and free diffusion takes place it would require 20 times as much acid to neutralize the alk. reserve of the plasma *in vivo* as is required *in vitro*. The largest amt. of acid injected (1200 cc.) was 10.6 times the amt. required to neutralize the alk. reserve of the blood plasma *in vitro*. This amt. of acid reduced the alk. reserve *in vivo* from 0.023 N to 0.0005 N.

A. P. LOTHROP

The fat content of embryonic livers. O. G. IMRIE AND S. G. GRAHAM. Univ. Toronto. *J. Biol. Chem.* **44**, 243-54 (1920); cf. *C. A.* **14**, 3711.—"In the latter part of embryonic life, it is normal for the fetal liver in guinea pigs to contain large amts. of fat. This fat has an I value as high as is normal in later life when a much smaller amt. of fat is present. This fat decreases in the first 48-72 hrs. after birth and then no more is found in the liver than later in life. The accumulation of the fat in the liver during the latter part of gestation, the unsatd. nature of the fat, and its rapid disappearance after birth suggest that it is material required by the young animal

after its communication with the maternal circulation has ceased. It is, however, possible that this fat is not utilized for the production of heat and energy but is transferred to the connective tissues after being converted into fat of the connective tissue type. If fat is mobilized experimentally by phlorhizin and fasting in pregnant guinea pigs, with embryos under 40 g. in wt., fat accumulates in the liver of the embryos but the fat is of the connective tissue type. When the embryos are above 40 g. in wt., and the fat is mobilized, more fat is found in the liver than otherwise, up to 30% of the fresh tissue, and this fat too is of the connective tissue type. It is impossible to say whether this fat is derived from the embryonic or maternal connective tissue fat. Fasting produces a fatty infiltration of the embryonic liver much more readily than in the maternal liver. If the fat were maternal in origin, it would indicate an avidity for fat on the part of the embryonic liver. The infiltration of fat in the embryonic liver may be quite independent of any similar change in the maternal liver."

A. P. LOTHROP

Studies on blood fat. I. Variation of the blood fat constituents of rabbits under normal conditions. YAJIRO HORIUCHI. Harvard Univ. *J. Biol. Chem.* 44, 345-61 (1920).—Detns. of the total fatty acids, cholesterol, and lecithin in whole blood, plasma and corpuscles of 19 normal rabbits were made using Bloor's methods with slight modifications. The content of fat constituents of whole blood and plasma in rabbits is less than in dogs and human beings but the difference in corpuscles fats is very small. In rabbit plasma there is $\frac{1}{3}$ as much cholesterol, $\frac{1}{2}$ as much lecithin and about $\frac{1}{4}$ as much total fatty acids as in human plasma. The ratios lecithin/cholesterol and total fatty acids/lecithin in rabbit plasma are, therefore, larger than in human beings. The content of fatty substances shows a racial and individual constancy and detns. made on successive days and at few weeks' interval gave values showing very little variation from the individual av. and from the 1st day's value. The ratios total fatty acids/lecithin and lecithin/cholesterol also show very little variation from the racial and individual av. and from the 1st day's amt. Even when 10 cc. of blood are taken daily, the fat content is practically const. provided the animal is not bled on more than 3 or 4 consecutive days; this is particularly true on a fat-free diet. If 10 cc. are drawn daily for a longer period, changes in the amt. of fat constituents occur.

A. P. LOTHROP

The diastatic ferments of the blood. D. SCLATER LEWIS AND EDWARD H. MASON. Royal Victoria Hosp., Montreal. *J. Biol. Chem.* 44, 455-63 (1920).—The diastatic activity of blood was detd. by the following procedure. Two 2 cc. samples were placed in 25 cc. flasks. To one were added 4 cc. of distd. H_2O and to the second 3 cc. The flasks were placed in a water bath at 40° and after the temp. had become const., 1 cc. of 1% sol. starch soln. was added to the second flask. After 15 min. the flasks were cooled, made up to the mark with Na picrate-picric soln. and the glucose was estd. by the method of Benedict. The diastatic index is expressed in terms of the % of sol. starch converted into glucose. The normal index was found to be between 14 and 25. The normal subjects (13) consisted of lab. workers, students and convalescent patients and furnished blood for 58 detns. The extreme variations were 7 and 29.4 but 47 of the 58 were within the range mentioned. "The diastatic activity of the blood shows very little change in relation to food. This applies both to ordinary meals and to those in which there is a large preponderance of one particular type of food. There is no const. increase in the blood diastase in diabetes and there does not seem to be any direct relation between the height of the blood sugar and the diastatic activity. Some of the most severe cases show the lowest diastatic activity. There is a marked variation in the level of the ferments in cases of nephritis but no evident connection between the type of disease and the diastatic activity and no const. relation between

the progress of the lesion and the diastatic index." The results obtained on diabetic patients are in marked contrast with those reported by Myers and Killian (*C. A.* 11, 1482), who found an almost const. increased diastatic activity which was more or less proportional to the blood sugar level and to the severity of the diabetes. A. P. L.

Experiments on carbohydrate metabolism and diabetes. III. The permeability of blood corpuscles to sugar. MARY B. WISHART. Rockefeller Inst. *J. Biol. Chem.* 44, 563-86(1920).—"No sp. alteration of the distribution of sugar between the blood plasma and corpuscles was found in the expts. with different quantities and modes of administration of glucose, different degrees of pancreatectomy and diabetes, lipemia, acidosis, exercise, cold, or different levels of the renal threshold. The concn. of sugar in the corpuscles is normally a little below that in the plasma. The discrepancy in favor of the plasma generally becomes greater as the blood sugar rises. These relations hold good in the several animal species examd. (dog, horse, goat, sheep), and in expts. *in vivo* and *in vitro*. The statement that in the declining stage of hyperglucemia the corpuscles retain sugar longer than the plasma was not confirmed. The concn. in the corpuscles rarely equals that in the plasma, and the finding of an excess in the corpuscles is probably to be interpreted as an analytical error. The term permeability as commonly used in relation to the sugar content of the corpuscles carries the idea that this is governed by a partially permeable membrane surrounding the corpuscle, and further that the soly. of glucose in the corpuscle substance is the same as in the plasma. This conception of permeability has received support from the assertions that the corpuscles take up and give off sugar more slowly than the plasma. It may possibly derive some support from the fact that washing in physiol. salt soln. changes the corpuscles in such a way that they take up less sugar. In view of the almost uniformly lower concn. in the corpuscles, however, and the quickness of adjustment on this basis whether the blood sugar rises or falls, it seems a more probable assumption that the coeff. of distribution depends upon the soly., glucose being more freely sol. in the plasma than in the corpuscle substance, perhaps because of the lipid content of the latter. Inasmuch as the sugar content of the corpuscles is subject to considerable irregularities from unknown causes and without known physiol. significance, plasma analyses should be preferred to those of whole blood for exptl. and clinical purposes. A. P. LOTHEROP

Studies of the distribution of carbon dioxide between cells and plasma. L. W. SMITH, J. H. MEANS AND M. N. WOODWELL. Mass. General Hosp., Boston. *J. Biol. Chem.* 45, 245-53(1921).—"Analyses were made of the CO_2 content both of whole blood and, after centrifugation, of the plasma. At the same time the proportion of cells to plasma in each sample was detd. by means of the hematocrit and the relative amts. of CO_2 in the cells and in the plasma of a unit of blood were calcd. therefrom. "As the blood passes from the arterial to the venous side of the circulation in normal man its cells gain from 4 to 11 vols. % of CO_2 . At the same time the corresponding gain in the plasma is only from 0.0 to 1.8 vols. %. The conclusion is drawn, therefore, that the transport of CO_2 is accomplished mainly by the cells. The same holds true in anemia and in certain other diseases, even though because of alterations in the cell vol. plasma vol. ratio the actual distribution of CO_2 between cells and plasma is altered." A. P. LOTHEROP

Relationship between cholesterol and cholesterol esters in the blood during their absorption. ARTHUR KNUDSON. Albany Med. College. *J. Biol. Chem.* 45, 255-62(1921).—See *C. A.* 14, 3704. A. P. LOTHEROP

A study of the distribution of iodine between cells and colloid in the thyroid gland. II. Results of study of dog and human thyroid glands. HARRY B. VAN DYKE. Univ. Chicago. *J. Biol. Chem.* 45, 325-32(1921); cf. *C. A.* 14, 2946.—In general, despite

great variations in the I content and morphology of the glands analyzed, the ratio of I concn. in cells to colloid-I concn. is relatively const. The ratio is not altered by the feeding of KI or free I for from 3 days to 3 weeks, although the total I content is greatly increased. The ratio for dog's thyroid is much lower and more constant than that of the beef or sheep.

A. P. LOTHROP

The diurnal variation in the size of red blood cells. CECIL PRICH-JONES. Cambridge Univ. *J. Path. Bact.* 23, 371-83(1920).—All the facts obtained suggest that the diurnal variations in the size of red blood cells are due to differences in the reaction of the blood. Expts. *in vitro* in which CO_2 , lactic acid, or Na_2CO_3 were added to defibrinated rabbit blood, showed that the red cells swell with an increase of acid and shrink with an abnormal alkalinity. The swelling of the cells in venous blood may perhaps be considered an arrangement for slowing the passage of the blood through the lungs until the CO_2 is gotten rid of. The author made simultaneous detns. of blood reaction and red-cell diam. on himself before and after short violent exercise. In each case here was a decrease in alkalinity and an increase in red-cell diam. After about 6 min. of forced breathing the mean diam. of the cell had diminished about 0.5μ . Subsequently, as the alkalinity of the blood returns to normal, the size of the red cells becomes normal. No means is known of judging whether the diminished alkalinity and increased diameters which prevail during the active part of the day are due to accumulation of CO_2 , or lactic acid, or to some other source of altered reaction.

JOHN T. MYERS

Transmission of the so-called diffusible serum salts through the placenta. F. EDELSTEIN AND A. YLPPÖ. *Z. Kinderheilk.* 27, 79-91(1920).—The serum of the mother and that of the child obtained from the umbilical cord at birth were tested for Na and K. The results indicate that diffusion of these salts through the placenta does not follow the osmotic law entirely but that the vital activity of the placental cells plays an important part as in the transmission of more complex substances—foodstuffs, antibodies, etc. The amt. of diffusible salts in fetal serum is greater than in maternal; Na, 0.385% to 0.353%; K, fetal 0.053%, maternal 0.04%. On the contrary, the amt. of alc.-sol. material in the maternal serum is greater than that of the fetal, 1.75% as compared to 1.23%.

G. H. SMITH

• SKYFARTH, CARLY: Neue Beiträge zur Kenntnis der Langerhansschen Inseln im menschlichen Pankreas und ihrer Beziehung zum Diabetes mellitus. Jena: G. Fischer. 104 pp. M. 22. For review see *Deut. med. Wochschr.* 47, 27(1921).

G—PATHOLOGY

H. GIDEON WELLS

Hyperglucemia in its relation to immunity. G. L. ROHDENBURG AND H. F. POHLMAN. Columbia Univ. *Am. J. Med. Sci.* 159, 853-66(1920).—Rats were fasted for 12 hrs.; a blood sugar detn. was then made according to the Epstein method and followed directly by subcutaneous injection of adrenaline-HCl, pituitary ext., saline exts. of dried thyroid, pancreas or liver. In a second expt. some gland of internal secretion (adrenals, spleen, thyroid, parathyroids, thymus, spleen, testes, ovaries) was removed either entirely or in part and 0.5 cc. of 1% peptone injected for the purpose of releasing glycogen. In a third expt. aminoacetic acid, urea, olive oil, oleic acid and glycerol were used. Rabbits were injected with typhoid bacilli and sheep red blood cells. From the expts. recorded it may be concluded that a temporary hyperglucemia accompanies the injection of a variety of org. and inorg. substances. The reaction type encountered is not specific for any given substance injected, nor can a reaction type be said to be distinctive of lack of function of any one of the endocrine glands tested. Repeated injections of the same substance cause a gradual rise in the blood

sugar parallel to the formation of agglutinins or lysins. Irregular fluctuations occur in the sugar content of the blood from day to day, but the trend is upward until the max. titer of antibody is reached, no glucemic reaction following the further injection of the substance used. Whether this hyperglucemia is due to temp. variations which are known to follow the ingestion or the injection of foreign protein, or whether it is due to the breaking up of protein which occurs in the process of antibody formation, cannot at present be definitely stated. The expts. here recorded show a phenomenon associated with the process of immunity which has hitherto escaped observation. An analysis of the hyperglucemia following repeated injections of the same substance indicates that the hyperglucemia is one which gradually increases in intensity up to a certain level of sugar concn. in the blood, that it keeps this level of intensity for a short period and then returns to a normal figure even though the immune bodies are still present in the blood. The expts. further suggest that the hyperglucemia which follows the injection of substances generally supposed not to be capable of inducing antibody formation (*i. e.*, fats, polypeptides) may serve as a method for testing the reactions of the body when neither precipitins, agglutinins nor lysins are demonstrable. From a practical standpoint the absence of a hyperglucemia after the injection of a given substance known to induce hyperglucemia might be taken to indicate the point of max. antibody production in the individual or animal in question.

H. V. ATKINSON

A chemical study of blood changes following Röntgen-ray treatment of leukemia. CHARLES L. MARTIN AND W. DENIS. *Am. J. Med. Sci.* 160, 223-33(1920).—In the more severe cases the non-protein nitrogen was extremely high; after treatment a gradual but steady fall was noted. In view of the fact that the creatinine values are invariably normal and that in the most severe case urea accounted for only 20% of the non-protein nitrogen fraction (instead of the usual 50%) the suggestion is made that in leukemia there is present, possibly as a constituent of the white cells, some nitrogenous constituent not accounted for in the present scheme of micro-blood analysis. The uric acid content of the blood was much increased, but a large diminution in the number of white cells which occurred as a result of treatment caused no appreciable decrease in this constituent.

H. V. ATKINSON

Blood sugar tolerance test as an aid in the diagnosis of gastro-intestinal cancer. JULIUS FRIEDENWALD AND GEORGE H. GROVE. *Am. J. Med. Sci.* 160, 313-23(1920).—There is present in carcinoma of the gastro-intestinal tract usually a rather characteristic curve of sugar tolerance which differs somewhat from that observed in carcinoma of other regions of the body. The curve of this affection usually presents a high sugar content even in the fasting state, followed by an initial rise up to 0.24% or higher within 45 min. after the ingestion of the dextrose remaining at this level for at least 20 minutes and at no time during this period falling below 0.20%. The sugar tolerance test is rather distinctive, so that it may render valuable assistance in a large proportion of cases as a means of differential diagnosis between carcinoma and other diseases of the gastro-intestinal tract. As positive curves occur equally whether cachexia exists or not, or whether the extent of the involvement be slight or great, the authors are under the impression that the results may be quite definite even in the early cases of the disease. The blood sugar tolerance test may be of considerable diagnostic help in obscure cases of carcinoma of the gastro-intestinal tract.

H. V. ATKINSON

Endothelial leucocytes in the urine suggesting typhoid infection. O. H. PERRY PEPPER. *Am. J. Med. Sci.* 160, 336-40(1920).—A report of one case. H. V. A.

Glucose tolerance test in chronic vascular hypertension. JAMES P. O'HARE.

Am. J. Med. Sci. 160, 366-9(1920).—Two cases approached a typical diabetic reaction, 11 were abnormal and 7 were normal. H. V. ATKINSON

Blood cholesterol in gastro-enterological cases. TRUMAN G. SCHNABEL. *Am. J. Med. Sci.* 160, 423-8(1920).—Blood cholesterol offered little practical diagnostic help in 60 gastro-enterological cases studied. H. V. ATKINSON

Hyperacidity. MARTIN E. REHFUSS AND PHILIP B. HAWK. *Am. J. Med. Sci.* 160, 428-33(1920).—Hyperacidity as discussed in this article does not refer to the subjective symptoms but to the objective finding of an actual increase of titratable acidity over normal. Evidence is deduced to prove that the normal individual elaborates acid figures as high as those commonly associated with pathologic syndromes, and in their experience no acid figures found in disease have exceeded the figures which the authors have obtained under certain circumstances in health. The acid finding during the digestion of certain foods in the normal stomach was found to be within the range which is accepted by all clinicians as abnormal. There is a group of normal individuals, approx. 40%, who constantly show the acid titration findings of so-called hyperacidity. It is essential that views on this subject be altered and that these normal findings be accepted first as a basis for the interpretation of pathological cases. The introduction of very high acidities (0.5% HCl) is followed by the activity of the autoregulatory mechanism which brings about a gastric optimum.

H. V. ATKINSON

Technic of agglutination. W. F. HARVEY. Central Research Inst., Kasauli. *Indian J. Med. Research* 7, 671-81(1920).—Expts. are given to show the effect of varying the time, temp., dilus. of serum and of suspension, nature of dilg., and of the suspending fluid and test receptacle. A plea for the fixing of a standard procedure to be used in agglutination is made. H. V. ATKINSON

New example of an anaphylactic immunity. MAURICE ARTHUS. *Arch. intern. physiol.* 25, 319-29, 331-44(1920).—An example of anaphylactic immunity is furnished by rabbits which have been subjected to a series of subcutaneous injections of the venom of *Crotalus adamanteus*. These animals have been made anaphylactic, because they give the reaction when a protein or a coagulating venom is injected into their veins; they are immunized because they react less vigorously than fresh rabbits when intravenous injections of *Crotalus adamanteus* are made, and they withstand doses of the poison that are fatal to untreated rabbits. This condition of anaphylactic immunity should be distinctly separated from the condition of immunity by anaphylaxis. If one repeatedly injects horse serum into a dog a state of anaphylaxis is produced which is succeeded by an immunity to reaction to further injections of horse serum. A serum immunity follows the serum anaphylaxis. If repeated injections of the venom of *Crotalus adamanteus* are made under the skin of a rabbit a state of anaphylaxis is produced analogous to that obtained in the dog treated with horse serum, which is also succeeded by an analogous condition of immunity. F. S. HAMMETT

Immunity and anaphylaxis are two biologically distinct states. MAURICE ARTHUS. *Arch. intern. physiol.* 25, 383-93, 394-410(1920).—Studies are reported on expts. with rabbits which tend to disprove the idea that all acquired immunity is preceded by an anaphylactic phase. This is demonstrated by the effects obtained when venoms are used and indicates that anaphylaxis and immunity are manifestations of 2 distinct biological states. A continuation of the expts. shows that the acquired immunity to the venom of *Crotalus adamanteus* is specific in contradistinction to the anaphylactic state produced by the same substance. F. S. HAMMETT

Scurvy among adults in Glasgow. W. J. RICHARD AND W. D. MACKINNON. *Glasgow Med. J.* 12, 336-42(1920).—A description of the occurrence, signs and

symptoms and treatment of the cases of scurvy in the Govan Poorhouse Hospital.

F. S. HAMMETT

The diet as a post-operative factor in gastro-intestinal disorders. LOUIS H. LEVY. *Med. Rec.* 94, 142-4(1921).—The dietetic treatment following operation for duodenal ulcer, gastric ulcer, and extragastric conditions should be based on the pathological condition of the stomach and duodenum. All foods possessing any stimulating or irritating action should be avoided. Liquid foods such as whey, strained gruels, lemonade, orange juice, plain or malted milk, chicken broth, creamed soups, etc., are indicated.

F. S. HAMMETT

The thyroid factor in tuberculosis. H. R. HANOVER. *Am. Med.* 15, 643-6(1920).—H. brings out the point that although the thyroid may be in good order in the initial stages of tuberculosis the action of the toxins produced by the disease tend to induce a primary condition of hyperthyroidism with its attendant symptomatology, which in turn yields to a condition of hypothyroidism through infiltration and other pathological processes.

F. S. HAMMETT

Hyperthyroidism. M. FORD MORRIS. *Med. Rec.* 99, 133-6(1921).—M. emphasizes the importance of diagnosing the condition in its early stages and uses the estn. of the basal metabolism, the adrenaline tests, and the glucose tolerance tests as a basis of a differential diagnosis between hyperthyroidism and early tuberculosis, neurasthenia, etc.

F. S. HAMMETT

The endocrines in gastric disease. TRUMAN G. SCHNABEL. *Penn. Med. J.* 24, 229-32(1921).—S. is of the opinion that endocrine dysfunction is occasionally accompanied by dysfunction and pathology of the stomach. This association is mediated not only through the autonomic nervous system but also through direct action; hence organotherapy should be tried in gastric disorders of the functional type. F. S. H.

Contribution to the study of gastric juice secretion. GEORGES HAYEM. *Bull. mem. soc. med. hop. Paris* 44, 1523-9, 1590-6(1920).—The presence of liquid in the stomach in the morning is indication of a gastropathy. When the sp. gr. is no more than 0.010 this liquid is purely secretory and of gastric and extragastric sources. It usually exhibits an increased peptic activity. When the concn. varies between 0.010 and 0.012 sp. gr. the indications are that it contains dissolved alimentary residues and tends to be hypochlorhydric. The former type is indicative of a hypersecretion, the latter of a retention.

F. S. HAMMETT

The permeability of the anterior surface of the human lens in certain pathological conditions. J. W. NORDENSON. *Skand. Arch. Physiol.* 40, 125-8(1920).—The presence of blood or pus in the human vitreous humor, or the condition of glaucoma simplex or absolutum, lowers the permeability of the anterior limiting layer.

F. S. HAMMETT

Opinion concerning kidney disease on the basis of war experiences. A. V. KNACK. *Vierteljahrsh. gericht. Med.* 60, 145-74(1920).—A rambling dissertation admitting of little definite conclusion on the incidence and progress of renal disorders during the war.

F. S. HAMMETT

Bacteriolytic substances of leucocytes. GENGOU. *Bull. acad. roy. méd. Belg.* 30, 993-9(1920).—On treating well washed rabbit or guinea-pig leucocytes, resp., with 0.01 N or 0.1 N soles. of HCl or lactic acid, substances are extd. from the polynuclears only, which have the power of rapidly transforming into granules the cholera vibrio, the *Vibrio Metchnikovi*, *B. typhosus*, *B. pyocyaneus*, *B. coli*, and Gärtner's bacillus, just as occurs within the leucocytes. Red cells, blood platelets and spleen cells do not yield these substances. The exts. are active only after neutralization, acid or alkali equiv. to 0.0033 N inhibiting the disintegrating action on the microbes.

The active substances are not identical with alexin (complement), and remain with the protein fraction. Since before phagocytosis can take place within the leucocyte its reaction temporarily becomes acid, it is held that the active substances, of colloidal nature, pass into actual soln. in slightly acid media, but can not unfold their disintegrating action until neutralization occurs, when they resume the colloidal state and are more easily fixed on the bacterial cell.

M. HEIDELBERGER

"Insensible perspiration" over cutaneous cicatrizations and the skin of paretic limbs. S. MASUMECI AND G. DI MACCO. Univ. Palermo. *Sperimentale* 74, 252-73 (1920).—The insensible perspiration at the surface of cicatrized lupus lesions is less than that of normal skin, being solely due to the diffusion of H_2O into the air, and not to the secretion of sweat glands, which are absent. In the skin of paretic limbs the insensible perspiration is greater than in the case of normal limbs, the same effect being produced in rabbits by section of the sciatic nerve, and in these cases also, diffusion and not glandular action furnishes the chief mechanism of the H_2O evolution, the vasodilatation due to the nerve lesions being the real cause of the increase.

M. HEIDELBERGER

Phagocytosis. XII. Modifications of phagocytosis caused by the action of dilute hydrochloric acid on bacteria. ANTONIO CALDERONE. Univ. Palermo. *Sperimentale* 74, 274-85 (1920).—Contact of *B. typhosus* with 0.02 N to 0.0025 N HCl up to 24 hrs. diminishes phagocytosis, while there may be an increase after that time. With concns. of 0.00125 and 0.001 N there is an increase with short exposures, but a decrease after 2 hrs. The initial depression with the stronger solns. is held to demonstrate the negative chemotactic properties of the bacterial chloro-protein complex, the final increase corresponding with the death of the bacteria.

M. HEIDELBERGER

Method of determining the appropriate dose of tuberculin for the individual tuberculous child. MYER SOLIS-COHEN. *Arch. Pediatrics* 37, 641-50 (1920).—The appropriate dose of tuberculin for the individual patient depends on the tuberculin hypersensitivity and tolerance, and may be as little as 0.000001 mg. and as much as 0.1 mg. in different patients of apparently the same type. The therapeutic dose may be detd. for each patient as the amt. which gives the minimal reaction when injected intracutaneously into that patient. In 19 cases, "initial doses varied from 0.00000001 mg. to 0.01 mg., and were increased 10 times to 120,000 times over periods of from 1 to 21 months, practically without producing an unfavorable reaction in any."

JOSEPH S. HEPBURN

Complement fixation test for syphilis: incubation for fixation at ice-box temperatures. JOSEPH W. SMITH, JR. U. S. Army. *Philippine J. Sci.* 17, 31-5 (1920).—The Wassermann test may be rendered far more sensitive and reliable by use of 2 antigens (simple alcoholic ext. of beef heart, and cholesterolized ext.) and by incubation at a temp. of approx. 8° for a period of 4 to 24 hrs. The reaction with the cholesterolized antigen may serve as a guide to treatment of known syphilitics, while the reaction with the simple alcoholic ext. antigen may be relied upon as a diagnostic test. Diagnosis of syphilis should never be made upon a single positive Wassermann reaction, but must be based upon repeated physical exams. and tests with the simple alcoholic ext. antigen.

JOSEPH S. HEPBURN

Keeping qualities of dried and pulverized vaccine virus. O. SCHÖBL. *Philippine J. Sci.* 17, 55-7 (1920).—The vaccine pulp obtained from a vaccinated animal was ground in a sterile mortar, spread aseptically over a large surface, dried rapidly over a hygroscopic reagent *in vacuo*, ground, again dried, and kept in a desiccator at room temp. Each week this powdered virus was used for the vaccination of a monkey, while a control monkey was vaccinated with fresh glycerolized vaccine. After keep-

ing for 4 months, the dried virus still gave a first-class "take" which could not be distinguished from that in the control animal. The dried virus may be kept in rubber-stoppered amber glass vials, or in sealed ampules, or in an open bottle in a desiccator; it is mixed with glycerol prior to use. The bacterial content of the vaccine pulp markedly decreased during the process of desiccation. First-class "takes" were also obtained with samples of the dried virus which were shipped from Manila to various places in the Philippine Archipelago, then back to the former city, and had been 25 days in transit.

JOSEPH S. HENBURN

The nature of hemolysins. J. T. CONNELL AND L. E. HOLLY. Univ. Mich. *J. Bact.* 6, 89-102(1921).—The authors have dealt with the hemolysins of two organisms, streptolysin and megatheriolysin, both of which are very powerful and occur early in the growth of the organisms. The former is only produced under special conditions and disappears after 24 hours. The latter is elaborated readily upon very simple media and remains active for weeks. This difference depends on the rate and abundance of growth. Artificial antigens were made, using the fat complex in the form of fatty acids and their salts which are characteristic of the streptococcus and of megatherium. They were prepd. in alc. soln. but the amt. of alc. was too small to have any hemolytic effect. The artificial antigens were not capable of producing as active hemolysins as were the bacteria. Neither natural nor artificial streptolysins yield satisfactory antilysins. Both natural and artificial megatheriolysins produce strong specific antilysins.

JOHN T. MYERS

Hemolytic fever. K. YAMAKAMI. Lister Inst. Lond. *J. Path. Bact.* 23, 388-98 (1920).—The transfusion of a perfectly non-hemolyzed, non-isolytic blood does not cause any appreciable temp. variation of the recipient. The intravenous injection of the animal's own blood or non-isolytic blood of other animals, hemolyzed with water, causes a febrile reaction similar to that produced by foreign proteins. Water when injected intravenously into rabbits causes a fever of typical form even when it is redistd. just before the injection. The fever is, therefore, not due to the contamination of the water with a pyrogenetic substance of bacterial origin, but is to be attributed to its hemolytic property. The relationship between the amt. of the injected water and the temp. variation is quite similar to that in the case of foreign protein injection.

JOHN T. MYERS

An experimental study of gastrototoxic serum. YONEJI MIYAGAWA. Imperial Univ. Tokyo. *J. Path. Bact.* 23, 462-76(1920).—Isogastrolysin is formed when stomach cells from one rabbit are injected into another rabbit, but its production is not so uniform as that of heterolysin. The rabbit against rabbit immune serum contains a specific gastrolytic factor for the guinea pig stomach cells, but it is uncertain and inconstant. There is no difference in the immune serum obtained by immunizing with the fundus gland area and the pyloric gland area. Both gastrotoxins act more strongly on the mucous membrane of the prepyloric part and gastric body near and on the lesser curvature than on any other regions. It is apparent that the rabbit and guinea pig stomach cells have similar side chains.

JOHN T. MYERS

The pigments of the adrenals. G. MARSHALL FINDLEY. *J. Path. Bact.* 23, 482-9(1920).—Lipochrome pigment is present in the adrenals of man and the fowl. In the latter the lipochrome is obtained directly from the food. In addition to carotin and xanthophyll there is probably present in the adrenal a third substance related to the lipochromes. A true lipochrome infiltration occurs in all conditions associated with cell depression. Melanin pigment is of endogenous origin, and is formed within the nucleus in chronic conditions associated either physiologically or pathologically with cell depression.

JOHN T. MYERS

Action and constitution of antigens. M. NICOLLE AND E. CÉSARI. *Compt.*

rend. 171, 739-41(1920).—This paper is chiefly comments on J. Duclaux's work, *Les Colloids*, (C. A., 14, 2882).

L. W. RIGGS

Action and constitution of antibodies. M. NICOLLE AND E. CÉSARI. *Compt. rend.* 171, 878-80(1920).—An interesting discussion of agglutination, coagulation, decoagulation and similar phenomena is given. No exptl. work is reported.

L. W. RIGGS

Cholesterolemia. A. CHAUFFARD, G. LAROCHE AND A. GRIGAUT. *Ann. médecine* 8, 69(1920); *J. Am. Med. Assoc.* 75, 1730.—An increase in the cholesterol content of the blood after a meal containing fat was far beyond the amt. of cholesterol ingested in the food, a fact which suggests an intraorganic synthesis of cholesterol from the fat eaten. The rise and fall of the cholesterol content of the blood was studied in many pathologic conditions, the results apparently indicating that cholesterol has an important antitoxic action and presides in some manner over the production of antibodies.

L. W. RIGGS

The Bordet-Wassermann reaction. P. NOBECOURT AND H. BONNETT. *Presse med.* 28, 745-48(1920).—The serums of 801 babies and 1185 women, submitted to the Bordet-Wassermann reaction, gave an av. of 4.38 and 4.0% resp. positive reactions. This is stated to be an approx. av. of syphilis among women and children. The anti-complement frequently found in the blood of the babies and most evident immediately after nursing, is eliminated if the blood is taken 6 hrs. after nursing. The serum was decanted from the clot and preserved on ice. The method of Calmette and Massol was used, checking with the Levatidi and Latapie method, after the natural hemolysis were measured. Antigens prepd. from the heart and liver of a syphilitic fetus were used. Neither antigen gave non-specific reactions. All positive reactions showed active or latent syphilis. Negative reactions were obtained in cases of hereditary syphilis and in women and infants showing hypophy, cachexia, and osseus dystrophia. In 90% of the cases the blood of the mothers and infants reacted parallel. In the cases disagreeing, more often the mother alone gave a positive reaction owing to the fact that syphilis was acquired after conception.

H. A. SHONLE

Hyper-uricemia in gout and gravel. A. CHAUFFARD, P. BRIDIN AND GRIGAUT. *Presse med.* 28, 905-6(1920).—Gout and gravel are both traceable to the urolytic insufficiency of the liver cell.

H. A. SHONLE

Effect of filling the lung with fluid, particularly by osmotic edema, on the respiration, circulation, and blood. ERNST LAQUEUR. *Arch. ges. Physiol.* 184, 104-33(1920); cf. C. A. 14, 2021.—Pulmonary edema in rabbits was produced by insufflation of physiol. saline or by small amts. of hypertonic solns. (1 cc. of 47% dextrose soln.) causing an "osmotic" edema. Respiration was not obviously affected, although exact measurement showed a loss in depth of respiration compensated by an increase in frequency. Changes in the heart beat were similar to those in asphyxia. The blood pressure was practically unaffected and there was no considerable obstruction to circulation. Blood concn. was increased in osmotic edema, the increase being relatively proportional to the amt. of fluid entering the lung.

G. H. SMITH

Cytological and chemical examination of sputum for the diagnosis of asthma and asthmatic conditions. F. BEZANÇON AND S. I. DE JONG. *Bull. acad. med.* 84, 253-7(1920).—The chem. aspect consists in the demonstration of albumin in the sputum. In acute pulmonary edema albumin is present in abundance; in asthmatics albumin is lacking; in phlegmonous catarrh with chronic bronchitis, albumin is found in minimal amts.

G. H. SMITH

Pure protein requirements of milch cows. NILS HANSSON. *Kungl. Landbruks-Akad. Hand. Tid.* 59, 261 - 92 (1920). — The question of pure protein

requirements of milch cows cannot be answered by the ordinary feeding trials. Conditions due to the war have raised the question: Is it possible to lower the protein requirements from the accepted normal, 65 grams digestible protein per 100 kg. live weight and 45 grams per kg. milk produced, to the minimum, 50 grams digestible protein per 100 kg. live weight and 40 grams per kg. milk produced. The digestibility of the protein was determined by solution in pepsin-HCl. Results of a number of experiments showed that the protein requirements are fully met under all conditions by feeding 65 grams pure protein per 100 kg. live weight and 45 grams per kg. milk produced, also that the minimum, 50 grams digestible protein per 100 kg. live weight and 40 grams per kg. milk produced are sufficient only for cows producing a large amount of milk with a low (3% or less) percent of fat, and only the first three or four months of the gestation period. The experiments showed that pure protein from hay can take the place of pure protein from oil cake only when the amount of feed does not exceed the capacity of the animal to utilize roughage. C. O. SWANSON

H—PHARMACOLOGY

ALFRED N. RICHARDS

The toxicity of mercuric chloride, and its solubility in aqueous alcohol. J. STANLEY LAIRD. Univ. Toronto. *J. Phys. Chem.* 24, 736-7(1920).—The soly. at 18° and toxicity of HgCl_2 in solns. containing from 10 to 51% by wt. of alc. were detd. The data show soly. as follows:

EtOH.....	0	10	15	20	25	30	40	51%
HgCl_2 in 100 cc....	6.24	5.63	5.43	5.15	5.08	5.86	7.58	11.8g.

There is a pronounced min. of soly. in 24% alc., corresponding closely to the max. toxicity observed by Paul and Kronig (*Z. physik. Chem.* 21, 448(1896)). A. L. B.

The action of ethyl alcohol on the organism. V. DUCCESCHI. Pavia. *Arch. ital. biol.* 70, 93-114(1920).—EtOH administered during some days to the dog produces constantly a marked hypercholesterolemia and a distinct increase of fatty acids in the blood. The phosphatide content is less markedly and constantly increased. There is a const. increase in the total fat of the liver which may amt. to 300% of normal; the cholesterol and dry residue are increased to a less extent. Adrenals show a const. decrease in cholesterol (av. 40%), a slight increase of total fat and dry residue. No characteristic or const. changes can be observed in lipid content of kidneys and testes. Two young dogs showed marked cholesterol increase in the kidney. These changes are favored by inanition. Human beings who indulge in alc. excess show an increase of blood cholesterol as compared with those who use moderation or abstain. An appendix gives the following toxic coeffs. of alc. beverages, detd. by F. Cafferata, by injection into the jugular vein of a rabbit; (expressed in terms of ccs. per kg. of body wt.): Amyl alc., 0.56; EtOH, 10; MeOH, 20; absinthe, 7; cana 8 to 40; whiskey, 10; cognac, 13 to 18; gin, 18 to 20; anisette, 18.5 to 20; peppermint, 20 to 23; kummel, 24.5; wines, 65 to 80; beers, 152 to 200. A. T. CAMERON

Adrenaline and its relation to the potassium and calcium ions. W. LIBBRECHT. *Arch. intern. physiol.* 25, 352-60(1920).—When the suspended heart is perfused with normal Ringer soln. to which adrenaline has been added to a diln. of 1:20,000,000 an increase in amplitude is obtained as well as an increase in rate. If Ca is absent or in excess adrenaline has no effect. When K is absent a passing stimulation is obtained and when K is present in excess adrenaline causes the heart to take up its automatic beat. The results are interpreted as indicating that the adrenaline sensitizes the cardiac cells to the action of the Ca present, or that it effects a Ca displacement. The non-effect, then, of adrenaline is explicable when Ca is absent on the basis of there being no Ca to be liberated by the adrenaline, and when Ca is in excess to the fact that any Ca dis-

placement is ineffective because of the excess. With regard to the K ions, when these are absent the adrenaline liberates Ca as usual and the contraction results because of the sensitizing action. When K is in excess, adrenaline in freeing the Ca produces a balanced K/Ca ratio and activity is re-established.

F. S. HAMMETT

Coagulating and anticoagulating venoms. B. A. HOUSAY AND A. SORDELLI. *Arch. intern. physiol.* 25, 378-82(1920).—The anticoagulating venoms *in vitro* destroy the cytozyme and by that fact prevent the formation of thrombin. The coagulating venoms produce their effect by their own coagulating activity and by their stimulation of the production of thrombin.

F. S. HAMMETT

The biological role of potassium for the heart. W. LIBBRECHT. *Arch. intern. physiol.* 25, 446-58(1920).—An extended criticism of Zwaardemaker's (*J. Physiol.* 53, (1920)) ideas of wide influence of minutely radioactive substances on physiol. processes.

F. S. HAMMETT

Localized tuberculosis treated by injections of the sulfates of the rare earths. H. GRENET, S. BLOCH AND H. DROUIN. *Bull. mem. soc. med. hop. Paris* 44, 1406-15 (1920).—A report of favorable results obtained from the use of the sulfates of the rare earth metals in the treatment of such localized tubercular lesions as: tubercular adenitis, cutaneous tuberculosis, erythematous lupus, osseous tuberculosis and rhinopharyngo-laryngeal tuberculosis.

F. S. HAMMETT

The exact status of the salts of the rare earths in anti-tuberculosis therapy. H. GRENET AND H. DROUIN. *Bull. mem. soc. med. hop. Paris* 44, 1427-31(1920).—A review concerning the value of the rare earth metal sulfates in the treatment of tuberculosis, indicating that up to the present the findings have been favorable.

F. S. HAMMETT

Daily subcutaneous injections of the nov-arsenicals. JEAN MINET. *Bull. mem. soc. med. hop. Paris* 44, 1475-8(1920).—M. is of the opinion, which is supported by his studies, that the best method of nov-arsenical therapeutics is the daily subcutaneous injection of small amts. of the drug combined with 4.7% glucose soln.

F. S. HAMMETT

Treatment of localized tuberculosis with the sulfates of the rare earths. L. RÉNON. *Bull. mem. soc. med. hop. Paris* 44, 1425-7(1920); cf. *C. A.* 14, 2661.—Localized tuberculosis is distinctly benefited by treatment with the sulfates of the rare earth metals, Dy, Ne, Pr.

F. S. HAMMETT

Adrenaline and quinine: their antagonism. A. CLERC AND C. PEZZI. *J. physiol. path. gén.* 18, 1174-81(1920).—See *C. A.* 14, 3725.

F. S. HAMMETT

Action of adrenaline on the cardio-vascular system of man. Difference in the physiological effect in health and disease. RENÉ PORAK. *J. physiol. path. gén.* 18, 1194-1202(1920).—The physiol. effect of intravenous or intra-muscular injections of adrenaline into normal man is the production of a hypertension of short duration, the course of the curve of which varies from one subject to another; just as each person shows an individual curve of fatigue so does each person react to adrenaline in his own way. The adrenaline test is hence a physiol. characteristic individual for the person. It is not surprising then that diseased persons may also give a normal reaction to adrenaline which makes very difficult any interpretation of the alleged differences in results obtained in various endocrine disorders.

F. S. HAMMETT

The slow intravenous administration of large doses of sodium citrate. HAROLD NEUHOF AND SAMUEL HIRSHFELD. *Columbia. N. Y. Med. J.* 113, 95-8(1921).—The slow intravenous administration of large doses of Na citrate given intermittently over a period of 10 to 15 min. is nontoxic both exptly. and in man. Massive doses up to 14 g. have been given to the latter. When the compd. is administered rapidly

fatalities may occur. The optimum dose for adults is 6 to 8 g. in a 30% soln. and 1 to 3 g. in greater diln. for children. All types of bleeding, internal as well as surgical, have been controlled by this treatment, owing to the shortening of the coagulation time and of the bleeding time. F. S. HAMMETT

Alcohol and precision. UNO TOTTERMAN. *Skand. Arch. Physiol.* 40, 107-16 (1920).—This study shows that the daily ingestion of 25 cc. EtOH for short periods lessens the precision with which a mechanical process can be carried out by man. The nature of the lessening of the precision seemed at times to partake of a decrease in ability as such, and at times to be a more rapid onset of fatigue. The EtOH was ingested in 25% soln. and not with the meals. F. S. HAMMETT

The action of chloroform and ether on the circulation in rabbits. Y. AIRILA. *Skand. Arch. Physiol.* 40, 241-65(1920).—An extensively reported study of expts. on the effects on circulation of toxic doses of CHCl_3 and Et_2O . The conclusion is that there is marked paralyzing effect of CHCl_3 on the heart. If cardiac massage be instituted the heart can frequently be restored to activity and circulation again induced. F. S. HAMMETT

Direct application of poisons to the spinal cord of the frog. C. G. SANTESSON. *Skand. Arch. Physiol.* 40, 266-70(1920).—A brief report of the effects on reflex activity of the application to the spinal cord of the frog of curare, morphine-HCl, quinine-HCl, cocaine-HCl, physostigmine salicylate, veratrine-HCl andaconitine-HCl. F. S. HAMMETT

The excretion of digitalis compounds. C. G. SANTESSON AND K. RICHARD EKSTROM. *Skand. Arch. Physiol.* 40, 271-84(1920).—These studies indicate that when digitalis preps. are subcutaneously or intravenously injected into rabbits there can be detected in the urine substances which give the characteristic color tests and physiological reactions of the active preps. These recoverable residues, however, are only present in very small quantities and represent but 1% of the total amt. originally injected. Accompanying these active principles there are large amts. of decompn. products which give Keller's test but do not exhibit any heart activity. No evidence of a fecal excretion of the products was obtained. F. S. HAMMETT

The action of quitenine and cinchotenine. MARIE DAUBER. *Z. exp. Path. Ther.* 21, 307-18(1920).—Quitenine, a carboxyl deriv. of quinine, was prepd. from the latter by oxidation with KMnO_4 . It was found that this compd. exerts practically no effect on frog muscle or nervous system. The action on the frog heart is of the same type as that of quinine, though somewhat retarded. On warm-blooded animals it exerts a toxic action on the kidneys, the acute lethal dose being 0.23 g. per kg. Cinchotenine when similarly tested showed a much lower toxicity on both cold- and warm-blooded animals. Rabbits withstand, without symptoms of harm, doses up to 1 g. It appears from these studies that quitenine exerts a specific toxic action on the rabbit kidney which is not exhibited by cinchotenine. Moreover, the parasitocidal activity of quinine is not shown by its deriv. quitenine to nearly the same extent, though the compd. is strongly toxic for both warm- and cold-blooded animals. Cinchotenine is almost completely non-toxic to both groups and apparently does not influence the metabolism of urea. When the compd. is reduced, however, it appears to be slightly more toxic. F. S. HAMMETT

Experimental and pathological-anatomical studies of the kidneys when poisoned by small doses of uranium. LASAR DUNNER AND KARL SIEGFRIED. *Z. exp. Path. Ther.* 21, 380-92(1920).—When very small doses of uranium salts are injected either subcutaneously or directly into the renal artery there occurs a more or less marked flushing out of N , NaCl and H_2O and the animal finally dies. The histological findings after subcutaneous injection showed only a marked flattening of the proximal

tubules. When the salt has been directly injected, however, a glomerula inflammation is produced. The hyperfunctioning of the kidney induced by these injections is not explicable on the basis of the pathol. findings. Apparently U exerts an elective action on renal function. F. S. HAMMETT

The microscopically determinable functional alterations in the capillaries caused by adrenaline. JOSEF KUKULKA. *Z. exp. Path. Ther.* 21, 332-40(1920).—K. studied the effect of adrenaline on the circulation in the capillaries of the nictitating membrane, the bladder, the pericardium, the lung, and the swimming bladder of frogs. He found that the drug caused a diminution of the size of the vessels which was accompanied by a striking crumpling of the walls. F. S. HAMMETT

Acute chromate poisoning. HEINRICH BRINGER. *Z. exp. Path. Ther.* 21, 393-408(1920).—A review of the literature on the subject and presentation of data from personal cases in which the toxemia resulted from absorption of $K_2Cr_2O_7$ from a salve used for scabies. Oliguria was an early consequence in all cases. The poison was found in the blood, urine, feces and stomach contents. F. S. HAMMETT

The influence of light from the mercury vapor quartz lamp on the resistance of the red blood corpuscles to hypotonic sodium chloride solutions. KONRAD VON ROHDEN. *Z. exp. Path. Ther.* 21, 444-57(1920).—When therapeutic doses of ultraviolet light are applied to man there occurs an increase in the min. and a deepening of the max. resistance of the red-blood corpuscles to hypotonic NaCl solns. This alteration in resistance does not occur in guinea pigs similarly treated. F. S. HAMMETT

Intraperitoneal administration of sodium bicarbonate solutions. J. W. EPSTEIN. Mt. Sinai Hospital, Cleveland. *Arch. Pediatrics* 37, 656-65(1920).—From expts. on rabbits, the following conclusions are drawn. A soln. of $NaHCO_3$ may be administered intraperitoneally; a 5% soln. may be used, but a 2% soln. is preferable since it is isotonic with the blood; the same results are obtained whether or not the soln. be treated with CO_2 . This mode of administration of $NaHCO_3$ may be used successfully in cases of acidosis of infants; the % of recoveries from the disease is then unusually high; and autopsies of cases which do not recover, fail to show any pathological effects as a result of the treatment. JOSEPH S. HEPBURN

• Effect of the inhalation of gases. G. A. WELSH. *J. Ind. Hygiene* 2, 328-32(1921).—The gases and vapors evolved during the manuf. of H_2SO_4 , HNO_3 , and cordite produce gassing proper if a sufficient amt. be inhaled at one time, and cause systemic poisoning if a given gas be inhaled in small quantities over a long period. The symptoms and treatment in industrial poisonings of both types are described; and the post-mortem findings are given for a fatal case of NO_2 gassing. JOSEPH S. HEPBURN

Arteriosclerosis produced by substances related to adrenaline. K. KIVONO AND K. HIGASHIHARA. *Kyoto Igaku Zasshi* 15, No. 6, 154-66(1919); *Jap. Med. Literature* 5, 46(1920).—Repeated intravenous injections of either ephedrine, or mydratine, or adrenaline into rabbits produced characteristic lesions, chiefly in the aorta, consisting of focal areas of necrosis of the elastic fibers and smooth muscle of the media. Adrenaline was the most toxic of the 3 compds. Rabbits which were either old or pregnant were readily affected; those which were young or were old but castrated were quite resistant. JOSEPH S. HEPBURN

Venom of the Philippine cobra (alupong) *Naja naja philippinensis*. C. MONSERRAT, O. SCHÖBL AND L. E. GUERRERO. *Philippine J. Sci.* 17, 59-64(1920).—The Philippine cobra (native name alupong or alimuranin) secretes a venom, which may be collected from live anesthetized animals as a thick, sirupy, colorless, opalescent liquid, and leaves a residue of small yellow flakes when desiccated *in vacuo*; an adult cobra yielded at one time approx. 0.052 g. of dry venom. The minimum lethal dose

producing death within 24 hrs. after subcutaneous injection, and expressed as wt. of dry venom per kg. of body wt., was found to be 0.0002 g. for the guinea pig, 0.0003 g. for the rabbit, 0.00008 g. for the monkey, and 0.0005 g. for the frog. It is calculated that the minimum lethal dose for man is 0.00019 g. of dry venom per kg. of body wt. (intermediate between monkey and rabbit). In the exptl. animals, the venom produced twitching of the lids, ears, and, at times, of the body muscles, excessive salivation, nausea, vomiting, loss of voice, rapid respiration, and drop in temp.; lachrymation and very marked ptosis of the upper eyelids also occurred, especially in monkeys. The animals showed marked weakness soon after inoculation; involuntary defecation and seminal emission immediately preceded death, which was due to cessation of respiration. The venom produced hemolysis of the washed erythrocytes of man, dog, rabbit, and guinea pig, but not those of sheep, cow and goat; it hemolyzed monkey erythrocytes with equal ease in the washed state or in the presence of the serum. The blood sera of certain vertebrates exerted an activating action on the hemolysis of the venom. An immune serum was obtained by subcutaneous inoculation of a horse with a soln. of the desiccated venom in physiol. saline; the first inoculation was made with 0.001 of a fatal dose, which is 0.025 g. for a horse; at each successive inoculation (made at intervals of 5 to 7 days) the dose was increased, and finally reached 0.1555 g. After immunization for approx. 8 months, the horse yielded a serum, of which 2 cc. protected guinea pigs from a double lethal dose of venom. After immunization for approx. 11 months, the serum of the horse was still richer in antivenom; when 0.4 cc. of the serum and a lethal dose of venom were incubated for 1 hr. at room temp., then injected subcutaneously into a guinea pig of 400 g. body wt., the animal was saved; intravenous injection of 1 cc. of the serum into a rabbit of 1 kg. body wt. protected it from a lethal dose of venom. The immune serum may be used subcutaneously in the treatment of cobra bite, injecting 10 cc. as a preventive, and 20 cc. (followed by another 20 cc., if necessary, 2 hrs. later) if symptoms of snake-bite poisoning have already set in. This is combined with the usual treatment of snake-bites.

JOSEPH S. HEPBURN

The toxicity of tetralin. LEWIN. *Z. deut. Oel Fettind.* 40, 439(1920); *Pharm. Zentralhalle* 61, 624.—The hydrogenated naphthalenes, used as solvents for resins, when given internally are excreted chiefly combined with glucuronic acid. A small amt. escapes through the lungs. Rabbits die from the administration of 5-6 g. tetrahydronaphthalene, narcosis first resulting. In man, the urine is colored a dark green and naphthalene, dihydronaphthalene, and α - and β -naphthoquinones are present in small amts. Hydrogenated naphthalene is moderately toxic to man. H. A. S.

Collection of radium emanation for therapeutic use (LIND) 3.

I-ZOOLOGY

R. A. GORTNER

Combating vermin by chemical means. RITTINGHAUS. *Z. angew. Chem.* 33, I, 280(1920).—Successful attempts at destroying moths by the use of aldehyde vapors are related. Aldehyde was generated by burning alcohol in a lamp whose wick was surrounded with a platinum cylinder, thus giving flameless combustion. W. C. E.

Results of experiments with miscellaneous substances against chicken lice and the dog flea. W. S. ABBOTT. *Bur. Entomology. U. S. Dept. Agr., Bull.* 888, 1-15 (1920).—In a study of the effectiveness of different insecticide ingredients in the control of chicken lice, tests were made with 22 coal-tar mixts., 5 proprietary and 2 home-made mercurial ointments, 45 of the common proprietary chicken-lice powders and 39 miscellaneous powders. The oil mixts. prepared from the coal-tar products were more or less effective, and also the proprietary and other powders when the active

ingredients, naphthalene, nicotine, pyrethrum, S and phenols, were present in sufficient amts. Of the miscellaneous powdered materials 26 were found to be ineffective. The most highly recommended of the materials examd. are NaF, S, mercurial ointment and fresh pyrethrum powder. The most effective preps. against the dog flea are fresh pyrethrum powder, finely powdered naphthalene or *p*-dichlorobenzene and the common emulsified coal-tar cresote preps. applied as washes. W. H. ROSS

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The detection of meat extracts and their substitutes by means of their content of nitrogenous compounds. KARL BECK AND ERNST MERRIS. *Arb. Reichsgesundheitsamt* 52, 223-52(1920).—The total creatinine content is of value in the identification of meat exts. H. V. ATKINSON

Report on maple products. J. F. SNELL. Macdonald College, Quebec. *J. Assoc. Official Agr. Chem.* 4, 157-69(1920).—No conclusive results were obtained on the desirability of adding H₂O to all maple products, boiling to 104° and filtering in the prepn. of the sample. Comparison of drying maple products at 70° in vacuum and at 100° in H₂O or an elec. oven was made with a study of the effects of the quantity of sample, and of spreading material—sand, pumice or asbestos and in case of sugars with no spreading material. The refractometer method for H₂O is probably best for sirups and drying 40 hrs. at 100° agrees closely (little higher). Results indicate oxidation of maple products takes place on drying for long periods at 100°. Concordant results were not obtained in a vacuum oven at 70°. The Winton and Canadian Pb nos. were studied and further work was recommended on these methods. H. A. LEPPER

Report on honey. SIDNEY F. SHERWOOD. U. S. Dept. Agr., Bur. of Chem. *J. Assoc. Official Agr. Chem.* 4, 170-1(1920).—The application of the method of the Winton Pb no. to distinguish honeydew honey from normal honey was found to be of no value. Slight values for the polarization of mixts. of honeydew and glucose (20%) and the small variation between them and those for honeydew honey, makes the polarization after alc. pptn. of min. value only in detecting addition of glucose. H. A. L.

* Report on coloring matters in foods. W. E. MATHEWSON. Bur. of Chem. *J. Assoc. Official Agr. Chem.* 4, 171-2(1920).—Several qual. tests for alkanet, annatto, carotin, anthocyan, cochineal, caramel and Brazil wood are given. H. A. LEPPER

Report on metals in foods. DAVID KLEIN. Ill. Dept. of Agr. *J. Assoc. Official Agr. Chem.* 4, 172-9(1920).—A volumetric method for Sn in foods proposed by W. B. D. Penniman was studied. The method, which is given, consists of extg. Sn with HCl, pptg. with Zn, dissolving in HCl (absence of air) and titrating with KIO₄. Results obtained by the method compare favorably with those of the tentative method (cf. C. A. 14, 3284). H. A. LEPPER

Report on cereal products. J. A. LECLERC. Bur. of Chem. *J. Assoc. Official Agr. Chem.* 4, 180-3(1920).—Results by collaborators show that the CaO vacuum method for H₂O in cereals gives results as good as those by the official method of drying in vacuum or H₂ at 100°. Dstd. H₂O containing 0.1% NaCl gives the same amt. of gluten as Washington tap H₂O; pure dstd. H₂O causes a large loss of gluten. The NaCl soln. is recommended for washing gluten. For sol. carbohydrates, 1% HCl is preferred as the medium of extn. Extn. (cold H₂O) for 45 min. at 5° and 10° gave the same results and 1½ hr. extn. at 10° gave considerably higher results. No definite conclusion was drawn on detn. of Cl but results of collaborators were concordant by gasoline or Et₂O extn. The use of a minimum of Ca acetate in ashing gave results remarkably close to those by the official method (cf. C. A. 14, 3283). H. A. LEPPER

Report on coffee. H. A. LEPPER. U. S. Dept. of Agr., Bur. of Chem. *J. Assoc. Official Agr. Chem.* 4, 211-6(1920).—Comparison of the Stahlschmidt (*C. A.* 11, 2375) and Fendler-Stüber (*C. A.* 8, 3599) methods for caffeine in coffee showed the latter to be easier of manipulation and quicker than the former, using 3 times as great a sample and yielding a very much purer caffeine. Collaborative results warranted the tentative adoption of the F. and S. method.

H. A. LEPPER

Report on baking powders. H. E. PATTEN. U. S. Dept. Agr., Bur. of Chem. *J. Assoc. Official Agr. Chem.* 4, 217-32(1920).—At $p_H = 3.3$ Fe will not be pptd. with the PbS deposited in the Wichmann method for Pb in baking powders. A procedure is suggested to obtain this condition in this method. Accurate results cannot be obtained under the conditions of the Wichmann method and the use of $HgCl_2$ does not increase the accuracy. Studies on the soly. of $PbCrO_4$ in soln. containing $AcOH$ and $K_2Cr_2O_7$ showed that under the condition of pptn. of the Wichmann method the loss of Pb due to soly. of $PbCrO_4$ is *nil*. The Bryan modification of the Corper electrolytic method for Pb in baking powder gave consistent and accurate collaborative results and is recommended for tentative adoption. A method for Pb proposed by J. R. Chittick was studied and further study recommended. The details are given of the 2 last named methods as well as of an electrolytic method for Pb proposed by R. A. Holbrook and R. H. McCreary in which a rotating cathode is used which operates directly in a phosphoric acid suspension of the baking powder without preliminary hydrolysis of starch.

H. A. LEPPER

Oxidation method for determining benzaldehyde and benzoic acid together. ANON. *J. Assoc. Official Agr. Chem.* 4, 254(1920).—Measure 10 cc. of almond ext. into a 100-cc. flask, add 10 cc. 10% $NaOH$ and 20 cc. H_2O_2 (U. S. P.) and place in a H_2O oven, covering with a watch glass. Heat 20-30 min. (5-10 after C_6H_5CHO odor disappears). Transfer to a separatory funnel, add 10 cc. H_2SO_4 (1:5) and cool. Ext. C_6H_5COOH with 25, 25, 20 and 20 cc. portions of Et_2O , wash the combined ext. twice with H_2O (5-10 cc.) to remove H_2SO_4 . Filter into a dish, dry overnight in a desiccator and weigh C_6H_5COOH . Multiply by 10, subtract 1.151 times g. of C_6H_5CHO (found by the tentative method) per 100 cc. of sample and difference equals C_6H_5COOH in 100 cc. of ext. This was adopted as a tentative method.

H. A. LEPPER

Qualitative method for coumarin in vanilla extract. WICHMANN AND DEAN. *J. Assoc. Official Agr. Chem.* 4, 254-5(1920).—Make 10 cc. of ext. alk. (10% $NaOH$), dil. with 15 cc. H_2O and ext. with 20 cc. Et_2O . Add a few cc. strong alc. KOH to the Et_2O ext. and wash with 10 cc. H_2O . Pour Et_2O on to 1 cc. 50% KOH in a test-tube, shake, evap. Et_2O , evap. H_2O over free flame and fuse KOH . If coumarin is present a greenish color develops which disappears when fusion of coumarin to salicylic acid is complete. Dissolve, melt, add a few cc. H_2O , acidify with H_2SO_4 , ext. with 5-10 cc. C_4H_4 . Wash C_4H_4 once with a few cc. H_2O . Test for salicylic acid in C_4H_4 with a few drops of $FeCl_3$. If no color develops add 1-2 drops $N/10$ $NaOH$ to neutralize traces of interfering mineral acids.

H. A. LEPPER

Method for alcohol in ginger extract. F. M. BOWLES. *J. Assoc. Official Agr. Chem.* 4, 255(1920).—Add 50 cc. of H_2O to 25 cc. of ginger ext., sat. with $NaCl$ and shake with 75 cc. petr. ether. After letting stand 10 min. draw off the lower layer into a 200-cc. flask, wash the petr. ether carefully, shaking moderately, with 50 cc. satd. $NaCl$ and add this wash water to the 200-cc. flask. After completing the vol. det. alc. in 100 cc. of filtrate by distn.

H. A. LEPPER

Report on dairy products. JULIUS HORTVET. State Dairy & Food Commission, St. Paul, Minn. *J. Assoc. Official Agr. Chem.* 4, 201-10(1920).—Collaborative results warranted the recommendation for the official adoption of the Roesse-Gottlieb method as modified for fat in malted milk and ice cream, the tentative adoption of the Harding-

Parkin method (C. A. 7, 1559) for fat in ice cream, and the official adoption of the Schmidt-Bondzynski method for fat in cheese. Results on H_2O in malted milk, dried milk and cheese varied widely (cf. C. A. 14, 3288).

H. A. LEPPER

Mixed butter. OTTAVIO BORELLO. *Annuario della r. stas. sper. di caseificio di Lodi* 1919, 19-22.—Two methods of prepn. are used. (1) Fused cacao butter is churned with a predetd. quantity of cream. A smoothing machine eliminates the lumps from the product, which is then kneaded. (2) The fused cacao butter is subjected to the action of the churn with a predetd. quantity of H_2O and by slow cooling of the mass kept in agitation the fat solidifies in minute particles resembling snow. This is kneaded with a calcd. quantity of butter. Analyses of samples of mixed butter gave the following:

	% H_2O .	% Fat.	% Lacteous substances.	Wollay number.
I.....	14.34	20.6
II.....	14.64
III.....	17.90	80.26	1.84
IV.....	13.14	85.10	1.76	21.4
V.....	17.30

ALBERT R. MERZ

Comparative study of the methods for the determination of fat in cheese. OTTAVIO BORELLO. *Annuario della r. stas. sper. di caseificio di Lodi* 1919, 23-51.—The Soxhlet extn. method and the methods of Gottlieb-Röse, Gerber and Schmid-Bondzynski were examd. and the conclusion was reached that the Schmid-Bondzynski method is preferable to all the methods proposed.

ALBERT R. MERZ

Methods for the chemical and bacteriological examination of ice-cream. JOSEPH L. MAYER. *J. Am. Pharm. Assoc.* 9, 777-8(1920).—A review is given of the methods found by M. to be satisfactory.

L. E. WARREN

The function and preparation of starters in oleomargarine manufacture. A. E. HOFFMAN. *Chem. Age* (N. Y.) 28, 417-8(1920).—Starters, mediums containing a majority of desirable bacteria present in an active condition, natural and com. are described with the method of prepn. which does not destroy the vitamins nor caramelize the sugar of the milk used. The importance of the starter in oleomargarine manuf. and the avoidance of abnormal fermentation are discussed.

H. A. LEPPER

• The healthfulness of hydrogenated fats for food purposes. Experiments with cottonseed, peanut, linseed and sesame oils. E. ROSE. *Arb. Reichsgesundheitsamte* 52, 184-209(1920).—These oils were found to be free from As and Ni and harmless.

H. V. ATKINSON

Some famine foods in Ahamedabad. G. J. PATHAK. *Agr. J. India* 15, 40-5 (1920).—New materials which have been utilized as famine food are *Bid*, or the rhizomes of the sedge *Scirpus kysoar*; *Thek*, or the rhizomes of the sedge *Cyperus bulbosus*; *Poli* of *pan*, or the inflorescence of *Typha angustata*, and the tubers and fruits of *poyana* (*Nymphaea stiltata*). *Bid* contains about 70% digestible carbohydrates and 8-10% protein. When used for human food the clods dug from the soil containing the rhizomes are left unbroken until thoroughly dried. The plant grows naturally in salt land. When properly dried and roasted it is used as a flour, as a substitute for wheat. *Poyana*, is the common water lily of the *mal*. For food the tubers are roasted in ashes in the same manner as potatoes, or are boiled as vegetables. The seeds are used as a flour. The dried tubers contain about 68% digestible carbohydrates and 15% proteins, the seed 70% carbohydrates and 11% protein.

J. J. SKINNER

The accumulation of carbon dioxide from strawberries in refrigerator cars. H. F. BERGMAN. *Science* 53, 23-4(1921).—The max. CO_2 content in the air of unventilated refrigerator cars of strawberries was 2.5%. This was lowered materially during icing. This accumulation of CO_2 is not sufficient to cause injury to the berries. J. G. P.

Some changes in Florida grapefruit in storage. LON A. HAWKINS AND J. R. MAGNESS. *J. Agr. Res.* 20, 357-73(1920).—The investigation is primarily concerned with the acid and the sugar changes; some data are given on the general appearance and attractiveness of the fruit. Fruit will apparently keep for a longer period in cold storage, for decay from microorganisms is less and shrinkage is reduced. Cold storage has an undesirable feature which is the breaking down or pitting of the peel at 40° F. or lower. Flavor improves in cold storage for the fruit is sweeter and the acid content lower. Bitterness decreases on storage, owing apparently to the breaking down of the naringin in the pulp. The fruit improves in taste more rapidly at high temp. than at low temp. for the changes take place more quickly. Expts. indicate that grapefruit does not deteriorate rapidly after removal from cold storage. Dry matter increases during storage. Shrinkage runs from 5-8% in cold storage to around 23% in warm ventilated storage. F. M. SCHERTZ

Insect control of flour mills. E. A. BACK. Bur. Entomology, U. S. Dept. Agr., *Bull.* 872, 1-40(1920).—Detailed directions are given for the control of insect pests in flour and cereal mills by fumigation with HCN, and by use of heat. Neither method injures the mill building or equipment or affects the baking qualities of the flour. W. H. ROSS

Presidential address (food and drug legislation). JOHN MCCRAE. *Proc. S. African Assoc. Anal. Chemists* 1920 (Sept.), 20-36.—A discussion. F. W. S.

Utilization of "cannarecchia" or "sorgagna" (*Sorghum halepense*). E. PANTANELLI. *Stas. sper. agrar. ital.* 52, 405-15(1919).—This plant (Johnson grass) can furnish hay in arid regions of a quality little inferior to forage buckwheat and of the compn.:

Gathered in				
	Sept. 1918.		July 1919.	
		Digestible.		Digestible.
H ₂ O.....	15.00		15.00	
Crude protein.....	6.58	44.6	8.43	48.9
Crude fat.....	1.25		1.85	
Non-nitrogenous.....	27.24		27.12	
Crude fiber.....	44.80	58.2	41.82	58.4
Ash.....	5.13		5.78	

The roots were gathered in July during growth of the plant, but before flowering; in October when the fruit was mature, and in January at the time of max. rest and analyzed with the following results:

	July.	October.	January.
H ₂ O.....	52.98	50.53	50.09
Reducing sugars.....	3.06	5.40	2.37
Total sugars.....	12.31	13.54	11.58
Sucrose.....	9.25	8.14	9.21
Dextrin.....	1.37	1.44	0.78
Starch.....	20.37	19.60	27.30
Plastic carbohydrate.....	34.05	34.58	39.66
Cellulose.....	5.40	5.66	5.88
Nitrogenous matter.....	3.22	3.88	2.06
Fat.....	2.18	2.04	1.42
Ash.....	2.80	2.75	2.45

They make good forage or can be used for making starch, or sirup for human consumption or for the manuf. of alc. ALBERT R. MERZ

The quality of silage produced in barrels. R. NEWTON. *J. Am. Soc. Agron.* 13, 1-11(1921).—Barrels were found to be quite suitable exptl. containers for silage

as judged by the appearance, odor, palatability and various chem. tests. Silage from barrels compared very favorably with silage from an ordinary farm silo. Corn, sun-flowers, oats, buckwheat and peas were used in the tests. Moisture, total acid, non-volatile acid, volatile acid, amino N and total N were detd. F. M. SCHWARTZ

A deficiency in heat-treated milks (DANIELS, LOUGHLIN) 11E. Sugar-cane juice clarification for sirup manufacture (DALE, HUDSON) 28. Bacteria concerned in the ripening of corn silage (HEINEMANN, HIXON) 11C.

KÖHL, HUGO: *Hilfsbuch der Bakteriologie in der Anwendung auf die Nahrungsmittel*. Wien and Leipzig: A. Hartleben. 408 pp. M. 16. For review see *Deut. Zuckerind.* 46, 17(1921).

Condensing milk. I. S. MERRILL. U. S. 1,365,055, Jan. 11. Milk is heated on the inner surface of a cylinder as it flows spirally and downwardly over the surface. The flow of the milk is retarded by a spiral rotating device adjacent the inner surface of the cylinder.

Apparatus for drying foods. J. G. GOODRUB and H. L. TRUBE. U. S., 1,365,909-10, Jan. 18. The material under treatment is heated by circulating currents of air which are independently heated.

13—GENERAL INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

HARLAN S. MINER

Procedure in cases of appeal. JULIUS EPHRAIM. *Z. angew. Chem.* 33, I, 283-6 (1920).—Under German patent law the appellant has the rights of a party to an action, and must be heard in all arguments and considered in all decrees concerning the process at law. The appeal must recite the facts upon which it is based. A conclusive allegation of all the facts to be considered within the time allowed for appeal is not demanded by the law. All allegations are to be judged according to their intent and purpose as well as on purely legal grounds. Three grounds for an appeal are (a) lack of novelty and non-patentability, (b) "double patenting," and (c) claims contrary to law.

W. C. EBAUGH

British progress in chemistry. WILLIAM MACNAB. *Chem. Met. Eng.* 23, 1254-6 (1920).—The problems of the industrial chemist are discussed and a closer cooperation between theoretical and technical workers and greater technical knowledge on the part of those conducting chem. industries are urged.

G. W. STRATTON

Procedure for the preparation of active hydrogenation metals within the liquid to be treated. A. BROCHET. *Bull. soc. chim.* 27, 899-901 (1920).—Expt. has shown that if an unsatd. oil, such as cottonseed, be heated in the presence of Ni formate and H₂ below 150° there is no decompn. of the formate nor hydrogenation of the oil. Furthermore, Ni formate is not reduced by H₂ under these conditions. Beginning with 160° and up to 270° there is decompn. of the formate and partial hydrogenation of the oil, under atm. pressure and without the presence of H₂ or any reducing agent supplied from without. In the presence of H₂ the mass resulting from the decompn. of the formate behaves as a very active catalyzer and enables oil to be hydrogenated at about 100°.

J. T. R. ANDREWS

Preparation of active hydrogenation metals. A. BROCHET. *Bull. soc. chim.* 27, 897-98 (1920).—Metals, especially Ni, obtained by calcination of their org. salts, such

as formate or oxalate, constitute active hydrogenation catalyzers. The decomposition is marked by the evolution of CO_2 and H_2 in about the theoretical proportions. It was noted that decomposition does not take place in the case of the formate until the temperature has reached about 200° . At 270° the reaction becomes violent. Higher temperatures are necessary to calcine the oxalate. The catalyst thus obtained is not spontaneously pyrophoric, though if a part is heated locally to incandescence in the presence of air the whole mass is quickly transformed into oxide. Iron reduced in this manner is a poor catalyst, a fact which lends additional weight to the belief that this weakness is inherent with the nature of the metal itself, and not due to its mode of preparation.

J. T. R. ANDREWS

The hydrides of naphthalene, anthracene, phenanthrene, phenol, and their derivatives. J. H. FRYDLENDER. *Rev. prod. chim.* 23, 719-24 (1920); cf. *C. A.* 14, 3231. —Review of work recently published in Germany including industrial methods of manufacture of tetralin and preliminary purification of the naphthalene, various patented processes for the preparation of derivatives of tetralin, transformation of naphthalene into anthracene and phenanthrene, applications of tetralin in the varnish and dope industry, defects of tetralin varnishes and methods of obviating them, hydrogenation of phenol to cyclohexanol and formation of acetic and formic esters of the latter which may be used as substitutes for amyl acetate and as solvents for nitrocellulose.

A. P.-C.

Comparative tests of lubricating oils. ANON. *Shale Review* 2, No. 8, 25 (1920). —Comparative tests made at the Univ. of Colo. by A. J. Hunter, showed that shale oil has better lubricating qualities, than products from refined natural petroleum.

A. H. HELLER

The handling of liquids in chemical works. J. H. WEST. *Chem. Age* (London) 3, 591 (1920). —See *C. A.* 14, 2280.

H. L. OLIN

Effect of fittings on flow of fluids through pipe lines. DEAN E. FOSTER. *Mech. Eng.* 42, 816-8 (1920); *Chem. Met. Eng.* 23, 1172 (1920). —Pipe-fitting equivalent tables and steam flow chart are given with illustrations of use.

W. C. EBAUGH

Drying by electrically superheated steam. J. KARRER. *Engineering* 110, 821-2 (1920). —Owing to the scarcity of coal in some sections of Europe during the war it was found profitable to use electricity as the source of heating energy in drying. In the method described, the air in the oven chamber is kept circulating by fans, and the water vapor driven off from the material is superheated; greater thermal efficiency was obtained than by drying with hot air. Excellent results were obtained in the drying of foundry molds and cores, and in drying peat and vegetables; vegetables dried in this manner retain their natural color.

DONALD W. MACARDLE

Distillation and rectification. L. GAY. Univ. Montpellier. *Chimie et industrie* 4, 735-48 (1920). —A general study of the continuous separation of a mixture of 3 constituents in 2 phases of given composition. The relations established in a previous paper for binary mixtures (cf. *C. A.* 14, 1479) are generalized to apply to the present case; and it is shown how, in the case of a perfect column, the compositions of the phases passing through the successive sections of the distilling and rectifying columns can be calculated. By means of algebra and graphs (plotted with trilinear coordinates parallel to the sides of an equilateral triangle, the apexes of which represent the respective pure constituents of the mixture) G. arrives at the notion of the limit-composition corresponding to infinitely long distilling and rectifying columns for a given intensity of heating. Owing to the great complexity of the problem, it was somewhat simplified by stipulating that the mixture had neither maximum nor minimum boiling point. But the graphs representing the composition of the liquid phases passing through the successive sections of the distilling and rectifying columns were still extremely complicated. A few rules governing the maximum and minimum amounts of heat required for the operation of the columns have been deduced. The results thus obtained will be applied

to the problem of sepg. a mixt. of benzene, toluene and xylene into its constituents in a practically pure state.

A. P.-C.

Causes and prevention of the formation of non-condensable gases in ammonia-absorption refrigeration machines. E. C. McKELVY AND AARON ISAACS. *Bur. Standards, Tech. Papers* 1920, No. 180, 10 pp.—One of the greatest difficulties encountered in operating NH_3 refrigeration machines is formation of gases, whose presence is indicated by increased pressures in the system, corrosion of metal, and high operating costs. O is usually absent, and when H is high N is low, and *vice versa*. Expts. with steel bombs containing liquids investigated showed that in the gaseous phase no harm resulted; a protective coating of Fe_2O_3 formed instead. Distd. H_2O at 130° gave almost negligible results, but at 170° showed corrosion and H production. Air-charged water under 50 lbs. pressure showed O reduction and severe corrosion. Aq. solns. of NH_3 gave similar results. Carbonates, acetates, etc., increased corrosion. From a detn. of CO_2 the action of a soln. could be predicted. If CO_2 is not over 0.003% corrosion is not marked. To remedy corrosive action of solns. $\text{Na}_2\text{Cr}_2\text{O}_7$ equiv. to 0.2% total wt. of NH_3 charge was used with complete success in plant operation. Thus presence of N indicates air leaks, and H indicates corrosion by NH_3 soln.

W. C. EBAUGH

Repairing iron leaching vats. C. FLURY. *J. Ind. Eng. Chem.* 13, 168(1921).—The bottom of a cyanide leaching vat containing numerous holes was repaired by covering it with a 0.25 in. layer of asphalt, then a layer of canvas and finally another 0.25 in. layer of asphalt.

G. W. STRATTON

The angle of slope (LANGHANS) 2.

ISAY, HERMANN: Die Lage der deutschen Patente in den früher feindlichen Staaten. Berlin: Verlag von Franz Vahlen. M. 7. For review see *Gummi-Ztg.* 35, 370(1921).

Recovering volatile solvents from air or other gases. S. S. SADTLER. U. S. 1,365,791, Jan. 18. Volatile solvents such as ether or acetone are recovered by absorbing their vapors in a mixt. of sperm-oil 50, lard oil 25, light petroleum oil 25 and alc. 2 parts which is afterward subjected to distn. to recover the absorbed solvent.

Utilizing liquefied gases. HEYLANDT GES. FÜR APPARATEBAU. Brit. 153,309, July 12, 1920. The supply of O from a body of the liquefied gas particularly for aeronautical respiration or engine supply or for use by fire brigades or hospitals is regulated automatically in accordance with the deficiency. For this purpose a valve on the vessel containing the liquid is set so that the amt. of gas delivered diminishes with increase of the external pressure. A suitable app. is specified.

Filtering gases. N. KLARDING. Brit. 153,263, Oct. 28, 1920. Blast-furnace and generator gases are purified by passage through agitated layers of granular filtering material, from which the dust is removed by a branch stream of the purified gas. A suitable app. is specified.

Refrigerating. B. THORNS. Brit. 152,898, Dec. 24, 1919. A soln. of NH_3 in H_2O or other soln. of a volatile substance is evapd. under reduced pressure in a closed tank and a part of the cooled liquor is circulated through a cooling chamber or other external circuit, while the vapors are passed into an absorber containing weak liquor, the strong liquor being returned from the absorber to the evaporator through an inter-changer, in which it exchanges heat with some of the cool weak liquor passing to the absorber. A suitable app. is specified.

Acid-proof vessels. W. E. WINDSOR-RICHARDS. Brit. 153,047, June 24, 1919. A mixt. of sand or powdered glass or quartz and clay with a soln. of Na silicate is used

for making acid-proof vessels. The mixt., with or without the addition of asbestos fibers, is pressed into molds. The resulting articles are impregnated with a bituminous liquid, as described in 3,364, 1915 (C. A. 10, 2137), or otherwise.

Storing inflammable liquids. V. SCHARNAGL. Brit. 152,672, Oct. 20, 1920. In a system for the storage of inflammable liquids, the space in the tank above the liquid is filled with air satd. with the vapor of the liquid, and the app. is so arranged that the pump will only function when the pressure in the tank is below atm., so that in case of leakage and consequent diln. of the satd. air, liquid cannot be drawn off. The reduced pressure also permits the formation of a highly charged mixt. of vapor and air at low temps. A suitable construction is specified.

Outlet-pipe from acid-tanks. F. W. DEJAHN. U. S. 1,366,170, Jan. 18. Mechanical features.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

Report on water. J. W. SALE. *J. Assoc. Off. Agr. Chem.* 4, 84-93 (1920).—Analytical data and suggested methods are given for the detn. of Ca and Mg, Mn, Ba and free and albuminoid NH_3 in waters containing sulfides. S. recommends (1) that Ba be detd. by weighing as BaCrO_4 or titration with iodide and thiosulfate; (2) that detn. of Mn by the Na bismuthate method be adopted as an additional official method; (3) that further study be given to a rapid method for detg. Ca and Mg; (4) and that further study be given to the detn. of free and albuminoid NH_3 in water containing sulfides, with view to modifying official method in this respect. There is need of methods for detg. Pb, Cu, Zn and Sn in waters and calcg. milligram equivs. of radicals found in H_2O with a view to their use in interpretation in water analysis. The following methods, recommended in 1916 for adoption as official, are recommended to be adopted as official this year: (a) detn. of Li, Na and K, (b) of turbidity, (c) of color, (d) of odor, (e) the Schulze-Trommsdorf method for detg. required O, (f) methods I and II for dissolved O, (g) detn. of sp. gr., (h) detn. of H_2S , (i) of temporary hardness, (j) of alkalinity, (k) of total hardness, (l) of permanent or non-carbonate hardness. Consideration should be given to the Gutzzeit method for detn. of As with a view to adoption as an additional official method. The official method for detn. of nitrate N should be revised.

G. C. BAKER

Turbidity standard of water analysis. P. V. WELLS. *Bur Standards, Sci. Papers* 1920, No. 367, 693-721.—The present turbidity standard in water analysis is inaccurate. W. suggests that all turbidity standards be prepared according to specification by the Bur. of Standards. It is possible that standard samples of dry powdered silica could be prepared uniform as to size of particle and certified samples furnished to water labs.

G. C. BAKER

Water supply researches. ALEXANDER HOUSTON. *Water Water Eng.* 22, 233-6 (1920).—A detailed report giving advantages and disadvantages of both rapid and slow sand filtration. Rapid sand filtration should be preceded by storage or coagulation treatment and followed by chlorination. Waters vary in ease of filtration. Tastes due to treatment with excess Cl are discussed.

G. C. BAKER

Damage to deep wells by sea water. W. P. MASON. *J. Am. Water Works Assoc.* 8, 59-74 (1921).—The problem involved is due to a proposal to cut through a neck of land with a canal 12 ft. deep which would carry sea water. This canal would be 1000 ft., or nearer to a large pumping plant. The water pumped at present is excellent. Results from wells similarly placed indicate that sooner or later the character of the supply will be affected by salt from the sea water. Its influence on sanitary data is

cited. On past data a considerable period of years would elapse before this contamination would become serious. Finally data seem to indicate that wells once contaminated by salt rarely, if ever, return to their original state. D. K. FRENCH

Result of stopping chlorination one day. RALPH HILSCHER. *Eng. News-Record* 85, 1288(1920).—Pittsburg, Cal., with a population of 5000, is supplied by chlorinated Sacramento River water. Disinfection was discontinued for one day to repair the Cl app. One hundred cases of typhoid fever developed. Duplicate machines are now recommended so that one might always be held in reserve. FRANK BACHMANN

Factors influencing ultra-violet light water treatment. RUSSELL D. SCOTT. *Eng. News-Record* 85, 1283-4(1920).—Expts. on a small scale with a single-bulb type machine rated at 120 gal. per hr. showed that color and turbidity lower the efficiency of the process. Thorough preliminary treatment to remove these ingredients is important. FRANK BACHMANN

Saving money by water treatment. P. M. LABACH. *Ry. Age* 17, 17(1921).—The Chicago, Rock Island, and Pacific R. R. has 54 water-softening plants for waters varying from 11 to 70 gr. per gal. hardness; 18 soda ash only, 24 intermittent, and 12 continuous, at an investment of \$305,587. There are 412 sources of water supply, 290 of which furnish water of over 10 gr. per gal. hardness. About 50% of water comes from wells, 25% from streams, 10% from reservoirs, and the rest from lakes. The 117 supplies from streams carry large quantities of silt during part of the year. From Aug. 1919 to 1920, 1,642,510,000 gallons of water were given complete treatment and 311,460,000 gal. partial. Total of 4,560,110 lbs. scale was prevented from going to locomotive boilers at a cost of \$97,458. This represents a net saving of \$358,552. Diagram of territory covered and prints of two plants are shown. R. C. BARDWELL

Comparison of various methods of water purification. WM. MACKLIN TAYLOR. *Chem. Met. Eng.* 24, 123-8(1920).—The zeolite method is recommended for laundries, textile mills, dyeing plants, chem. manufactures, etc., where Na salts have no injurious effect and where the raw water lends itself to such treatment; pptn. softener methods should be used if water cannot be handled by zeolites. The pptn. water-softener is the only satisfactory method for the manuf. of ice. In large installations, with av. hard water which shows no tendency to foaming and priming, for fire-tube boilers, the pptn. water-softener gives best results. Boiler compds. are best where high amts. of Na salts tend to cause foaming and priming. Zn-bearing boiler compounds frequently correct electrolytic corrosion. G. C. BAKER

Design of aspirators for sterilizing water. A. E. WALDEN. *Mech. Eng.* 42, 562-4(1920).—A general discussion of different types of aspirators for uniting water with O₂ or air. The type adopted was of cast iron, enameled with the best possible white porcelain; but even this is subject to deterioration owing to high O₂ concn., which shows effects after about 5 years of operation. G. C. BAKER

Hardness of surface waters of the U. S. W. D. COLLINS. *J. Ind. Eng. Chem.* 12, 1181-3(1920).—A general account of the hardness of surface waters of the U. S. Soft water is found along the Atlantic, E. Gulf of Mexico, and Pacific coasts, and along the northern boundary states. Hard water is found in middle west states bordering the Mississippi and to the east. Hard and strongly alk. water is found in the area outlined roughly by N. Dakota, Arizona, Louisiana, Texas, Arkansas and southern part of California. Analyses are given. G. C. BAKER

Improvements in mechanical filtration. ANON. *Water Water Eng.* 22, 342-4(1920).—A general description of the Candy type of pressure and gravity filters. Washing with less water and increased rates of filtration are claimed. G. C. BAKER

The use of phosphoric acid in water softening. C. P. HOOVER. *Eng. News-Record* 86, 81(1921).—P₂O₅ is manufactured from phosphate rock by the action of

H₂SO₄. It is fed to the water at a rate of 0.7 gr. per gal. Many expts. have been tried to carbonate the softened water to prevent incrustation of sand grains and pipelines, but the P₂O₅ treatment appears to be the most satisfactory. FRANK BACHMANN

Operation of continuous type lime-soda ash water softener. R. F. CATHERMAN AND H. C. FISHER. *Chem. Met. Eng.* 23, 526-8(1920).—Analytical data, interpretation of results, and calcn. of lime and soda ash charges are given. Expts. were run using NaOH with satisfactory results. G. C. BAKER

Water softening with permutite. R. MEZGER. *J. Gasbel.* 63, 644-8(1920).—M. traces the development of the process and gives exptl. data obtained from examn. of water at Stuttgart. The tests show that it is possible by this method to remove hardness due to magnesia and thus prevent the formation of boiler scale. J. L. W.

Permutite. H. VOGTHER. *Z. angew. Chem.* 33, I, 241-3(1920).—A general review of the history and development of base-exchange processes. V. concludes that the active exchangeable bases are embedded in the porous structure of the zeolites, in whose fine capillaries the exchange action takes place. The silicate itself, whether composed of silica alone or in combination with alumina or iron oxide, does not play any function in the exchange of bases except to furnish a medium of suitable physical nature. Methods of prepn., and phys. and chem. properties are given. Patents are referred to. G. C. BAKER

Water softening with lime. W. HERBIG. *Z. angew. Chem.* 33, I, 237-8(1920).—A brief discussion of the general types of industrial installations for softening of water with lime. In pointing out the importance of obtaining a satd. lime soln. H. notes the influence of temp. and suggests a method of application to give best results. G. C. BAKER

Too low salt concentration in boilers is not economical. R. J. C. WOOD. *Elec. World* 77, 262(1921).—A concn. of 200 grains per gal. (3.4 g. per l.) is satisfactory as regards priming. The most economical operation results when there is the least amt. of blow-down consistent with absence of concn. trouble. A table shows blow-down losses with different boiler concns. W. H. BOYNTON

Comparative costs of drifting and slow sand filters at Toronto. JAMES MILNE. *Eng. Inst. Canada* 1921; *Eng. Contr.* 55, 138-9(1921); *Can. Eng.* 40, 194-5(1921).—The cost of the slow sand filter was \$934,404 and of the drifting sand \$1,090,811, for capacities of 32 and 50 mil. gal. per 24 hr. or per mil. gal. for construction \$29,200 and \$21,817. The annual cost has been for administration, operation and maintenance per mil. gal. \$7.29 and \$11.57, resp., and for interest charges \$6.50 and \$6.20, resp., for the slow sand and drifting sand. The drifting sand costs can be reduced by cutting the use of Al₂(SO₄)₃. The conclusions are given in detail. LANGDON PEARSE

Conservation of the quality of water of N. Y. State as a national resource. WM. F. WELLS. *Science* 52, 279-84(1920).—A warning with reference to contamination by trade waste. G. C. BAKER

Recent research work of Houston on mechanical filtration. *The Surveyor; Can. Eng.* 39, 581-2(1920).—This is a discussion of the 13th Research Report of the Metropolitan Water Board (London). The need of expert engineering guidance in handling the London expts. is pointed out. The work of Houston is criticized for the exceedingly small scale, and lack of engineering knowledge. LANGDON PEARSE

Operating the St. Louis filters. *Ann. Report Water Board 1920; Pub. Works* 50, 10(1921).—The important work was cleaning the filter sand, gravel and plates. A few broken strainer bolts and plates were found. The coating on the sand was 2.14% by wt., largely CaCO₃. The cost was \$266 per filter of 1400 sq. ft. area. L. P.

Water supply of Bluefield. E. S. TISDALE. *Pub. Works* 49, 569(1920).—Bluefield takes the major portion of its water from springs in a limestone formation. It is treated

with 0.2 p. p. m. liquid Cl. T. recommends connecting all houses on watershed to city sewers.

LANGDON PEARSE

Saskatchewan's water supply project. HAMILTON BUTLER. *Can. Eng.* 41, 111-2(1921).

LANGDON PEARSE

The water supply of Barranquilla, Columbia, South America. GEORGE C. BUNKER. *Eng. News-Record* 86, 10-1(1921).—Water from the Magdalena River is chlorinated and pumped directly into the mains. Excess water flows into a 900,000 gal. reservoir reserved for fire protection. Pumping is intermittent and requires installation of individual service tanks of sufficient size to supply water during non-pumping periods. The water is very turbid and a filter plant is being projected. Epidemics of dysentery are frequent and the death rate of children has been extremely high. FRANK BACHMANN

Relation of raw water to endemic typhoid fever. N. J. HOWARD. *Mun. Eng. San. Rec.* (England) 1920; *Can. Eng.* 40, 139-41(1921); *Pub. Works* 49, 567-9.—After discussing the general reduction of typhoid in municipalities where water purification and sterilization plants are installed, H. points out the failure to isolate typhoid in raw water in Houston's expts. in England. The conditions at Toronto are then noted in detail; the reduction in typhoid fever death rate was from 40.8 in 1910 to 2.0 in 1920. The seasonal prevalence of *B. coli* is shown to have a relation to the typhoid, the highest *B. coli* occurring in July, Aug. and Sept., the most typhoid cases also occurring then, following the worst water. The general improvement in sanitary conditions has also helped.

LANGDON PEARSE

Chlorine-binding compounds in water and sewage. VICTOR FROBOESE. *Arb. Reichsgesundh.* 52, 211-22(1920).—The capacity of water and sewage to decompose hypochlorites is of value in addition to its oxygen-consuming power with permanganates.

H. V. ATKINSON

Sewage disposal in S. Africa. A. E. SNAPE. *Engineering* 110, 580(1920).—It is impossible to discharge sewage into streams for they are dry many months of the year. In addition a law prohibits discharge of effluents which will destroy the quality of water for domestic use. The sewage is very concd. It passes through screens and grit chamber to remove floating material and heavy mineral matter. It then passes to a sedimentation tank where suspended solids are removed. The effluent passes on to land and is utilized for growing crops. Sludge from the sedimentation tank is passed into septic tanks where foul liquor is removed and run off on specially prepd. land. Sludge is dug out and dried in the sun. The odor is insignificant and entirely local. Dried sludge contains 3% N, and is utilized as fertilizer. Alfalfa is especially suited for cultivation on sewage farms.

G. C. BAKER

Simple system of sewage disposal for isolated dwellings. H. R. CROHURST. *U. S. Pub. Health Bull.; Eng. Contr.* 55, 128-9(1921).—The design is a simple rectangular tank, based in general on 4 cu. ft. (30 gal.) per capita. This should not be smaller than 94 cu. ft. A siphon dosing chamber is recommended. Open-jointed tile underdrains follow the tank, laid in the ground if sandy, or in prepd. sand or cinder beds, in amounts varying from 20 to 100 ft. per capita, according to soil.

L. P.

Note on purification of sewage by the activated sludge process. LUCIEN CAVEL. *Compt. rend.* 171, 1406-7(1920).—The NH_3 content of sterilized sewage remained const. upon aeration, but when inoculated with activated sludge the NH_3 was completely oxidized to nitrite and nitrate in 24 hrs.; this shows the necessity of bacteria for purification. C. notes the effect of Fe and finds that purification does not take place under acid conditions. The effluent from sewage purified by activated sludge contains bacteria essential for purification.

G. C. BAKER

Activated sludge. Symposium. *Eng. Inst. Canada* 1921; *Can. Eng.* 40, 193-4(1921).—After a general discussion, Wm. Gore describes expts. at Toronto in which the

sewage is settled with digested sludge and then aerated. The air used has average $3/8$ cu. ft. per gal. based on 10 ft. depth and 4 hr. period. The sludge is different, drying readily. The need of operating supervision is urged. LANGDON PEARSE

New activated sludge experiments at Stoke-on-Trent. W. H. MAKEPEACE. *Can. Engr.* 40, 172-3(1921).—The sewage of the Tunstall district contains pottery wastes. The existing works were remodelled into a detritus tank 9×21 ft. \times 5 ft. 6 in. deep (6,700 Imp. gal.), an aeration tank 75×42 ft. 9 in. \times 7 ft. 9 in. deep (156,875 Imp. gal.) and a sedimentation tank 25 ft. diam. \times 13 ft. $10\frac{1}{2}$ in. deep (42,500 Imp. gal.), with double-flow inlet and sludge scraper. Air used varied from 1.1 to 0.64 cu. ft. per Imp. gal. at a pressure of 4 lb. per sq. in., the diffusers being in furrows. The plant was worked on a continuous basis from 120,000 Imp. gal. per 24 hr. up to 300,000. The vol. of sludge was 70% after 3 hr. settling. The sludge contained 4.5% N. With additional tank capacity up to 3 times the amt. of dry flow was handled. Thorough pre-settling was required to remove the heavy pottery waste of sp. gr. 2.5. L. PEARSE

Test of Trent activated sludge devices at Pasadena (California). R. V. ORBISON. *Eng. News-Record* 85, 1286-8(1920).—The Trent process consists of aeration and agitation of the sewage by pumping sewage and air into the bottom of the activation tank. Distribution is by means of revolving perforated arms on the revolving lawn sprinkler principle. The tests proved that the process was too erratic, not dependable, and that it required an air blower and a sludge reaeration tank with filtrose plate. The process made a fair showing with the older activated sludge process but it took twice the time and cost more to operate. FRANK BACHMANN

Notes on English sewage treatment. THORNDIKE SAVILLE. *Pub. Works* 50, 24-6(1921).—Notes are given on a trip made in July to Sept., 1919. At Bradford, with a wool industry, the sewage is treated with H_2SO_4 . The dry sludge contains 2% N. At one time SO_2 was tried but abandoned. At Huddersfield with tanks and sprinkling filters, the sludge is treated with H_2SO_4 , dried and the grease extd. The cake contains 3.5% N. At Morley the wool waste sewage is treated with H_2SO_4 . The sludge is pressed, and the grease extd. The cake is sold. At all 3 places the grease rarely falls below 30% in the dried sludge. The activated sludge expts. at Manchester are interesting for the intermittent application of air; 1.28 cu. ft. per gal. sewage are used. At Sheffield, the activated sludge expts. were successful; only agitation is used. At Birmingham sep. sludge digestion is carried on. LANGDON PEARSE

Relation of chemical engineering to sewage and trade waste treatment. R. H. EAGLES. *Chem. Met. Eng.* 23, 438-40(1920).—A brief outline of sewage and trade waste treatment, with special reference to the activated sludge process and the chem. engineering problem involved in pressing and drying the sludge. Considerable attention is paid to plain sedimentation. G. C. BAKER

Further study of the excess oxygen method for the determination of the biochemical oxygen demand of sewage and industrial wastes. EMERY J. THERIAULT. U. S. Public Health Repts., Reprint No. 594, 1-29(1920).—Biochemical O-demand methods involving the addition of nitrates or the use of stability number relations are open to objection. The excess O method yields accurate results with as little labor as is required by other methods. The method is well fitted for lab. studies. Digestion for 5 days seems to give values sufficiently accurate for most purposes. A method is suggested for reducing the period of incubation to 2 days. It gives good results when applied to industrial wastes. The main errors of the method are largely due to the use of improperly adjusted dilg. water or occur in making dilns. The method consists in dilg. a known vol. of waste with a definite vol. of water of known O content, and after incubation, detg. the residual O. The method, with app. required, is described in detail. G. C. BAKER

Practices of waste disposal from war manufactures. H. STROOFF. *Chem.-Ztg.* 44, 597-8, 601-3(1920).—The article deals with disposal of wastes from powder and explosives factories, and iron and metal works. S. advocates the removal of the solid material from powder and explosive wastes by sedimentation or sedimentation and filtration followed by neutralization of the waste acids with lime. The pptn. of Fe in waste from metal works with lime is advocated. The pptd. $\text{Fe}(\text{OH})_3$ is allowed to settle and the supernatant liquid removed. S. urges treatment of such wastes of industrial plants during peace times, and points out dangers if left untreated. G. C. BAKER

Disposal of trade wastes. R. S. WESTON. *Am. Soc. Mun. Impet.* 1920; *Pub. Works* 49, 504-6.—Trade wastes are classified by (1) excessive suspended matter content; (2) deposits in sewers; (3) excessive fats and org. matter; (4) waste mineral oil; (5) free acid; (6) chemicals inhibiting biological purification, (7) starchy or saccharine contents which ferment, producing acid inhibiting nitrification. The treatments required are illustrated by the tannery industry at Peabody, Mass., where Dorr screens and thickeners have been installed; the use of centrifugals on wool-scouring waste at Hudson, Mass.; the neutralization of acid wastes by lime; the effect of Cu and As on sewage, as studied for Cu at New Haven; the treatment of cane and beet sugar wastes, and lactic acid wastes. LANGDON PEARSE

Sanitation at Lethbridge, Alta. H. W. MEECH. *Can. Eng.* 40, 106(1921).—A description of the water filtration, sewage treatment, garbage collection and general lab. carried on in Lethbridge. LANGDON PEARSE

Is chemical denitrification important for agriculture and for water analysis? (SCHERINGA) 15. Standardization of laboratory methods (WADSWORTH) 7. Graphic representation of analytical results (GRAU) 7.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Is chemical denitrification important for agriculture and for water analysis? K. SCHERINGA. Utrecht. *Pharm. Weekblad* 57, 1481-3(1920).—The reaction between nitrites and NH_3 or its salts, with elimination of N, is catalyzed by methyl red, malachite green and fluorescein; but it is inhibited by many org. substances, particularly colloids. This probably explains the simultaneous presence of salts of NH_4OH and of HNO_3 in many natural waters. Sterile soil has a very pronounced inhibiting effect. The reaction may occur to some extent in manures, with consequent loss of N; but the protective presence of inhibiting substances is so common in nature that denitrification due to this cause is nearly negligible. JULIAN F. SMITH

Acidity of Japanese acid clay. KIUHEI KOBAYASHI. *J. Chem. Ind. (Japan)* 23, 543-9(1920).—Japanese acid clay (Japanese fuller's earth) has the compn. $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot x\text{H}_2\text{O}$, and is probably a mixt. of colloidal hydrous Al silicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$) and an amorphous compd. of ortho-silicic acid ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) containing certain basic compds. as impurity. The reason why this clay should give an acid reaction was investigated by K., who found *no true acid substance in the clay itself*. The conclusion is that the acid reaction on blue litmus paper or other indicators is due to free mineral acid liberated by adsorptive action of this clay. When it is added to some basic dye (R-Cl), then there may be supposed the existence of a so-called Helmholtz's double layer on the surface of the clay and that the clay adsorbs OH^- according to its property as an acid gel, H^+ being thus liberated. R combines with OH^- and H^+ unites with Cl⁻ of the dye. In a similar manner, when the acid clay is added to neutral KCl soln., it adsorbs K^+ ,

and HCl will be formed, which in turn dissolves Al of the clay. Subsequently $AlCl_3$ is hydrolyzed to $Al(OH)_3$ and HCl. K. observed that silk or wood fibers also change blue litmus paper to red, and concludes that these fibers must act in a similar manner as the clay. S. T.

Acid clay and acid soil. KIUREKI KOBAYASHI. *J. Chem. Ind. (Japan)* 23, 549-55 (1920).—A review of different theories on acid soils is given. According to K., acid soil contains acid clay (cf. preceding abstract), which has adsorptive action on the neutral substances, rendering the soil acid without involving chem. reaction. S. T.

Six years' experience in improving a light unproductive soil. BURT L. HARTWELL AND S. C. DAMON. *J. Am. Soc. Agron.* 13, 37-41 (1921).—The expt. was carried out on a Warwick sandy loam in Rhode Island. Liming and the use of P together with the use of legumes for collecting N and increasing humus are advocated. F. M. S.

Need of nitrogen for hay-land. PEHR BOLIN. *Kgl. Landbruks-Akad. Handl. Tid.* 59, 401-16 (1920).—Hay-land, with the exception of pure clover, showed a positive need of N, applied in the form of nitrates, in addition to the need for P and K. C. O. SWANSON

The lime question in the light of recent soil investigations. HARALD R. CHRISTENSEN. *Kgl. Landbruks-Akad. Handl. Tid.* 59, 331-4 (1920).—A general discussion of the relation of lime to various soil problems, phys., chem. and biological. C. O. SWANSON

Phosphorites, superphosphates, tetraphosphates. A. QUARTAROLI. *Stas. sper. agrar. ital.* 52, 416-35 (1919).— $Ca_4(HPO_4)_2$ occurs in 2 forms having very different chem. properties. These may be schematically represented by (1) $|Ca|Ca|(HPO_4)_2$ and (2) $|Ca|Ca|(HPO_4)_2$. (1) is amorphous (obtained by treating H_3PO_4 with the desired quantity of $Ca(OH)_2$ or pptg. a Ca salt with Na_2HPO_4) and transformable into $Ca(H_2PO_4)_2$; (2) is cryst. (obtained by the slow spontaneous decompn. of a satd. soln. of $Ca(H_2PO_4)_2$) and is not transformable into $Ca(H_2PO_4)_2$. (1) is rendered sol. on addition of sufficient strong acid to sat. 1/2 of the combined Ca according to the reaction $Ca_4(HPO_4)_2 + H_2PO_4 = 2Ca(H_2PO_4)_2$ (HCl or H_2SO_4 may be used); (2) requires almost double this quantity since it is rendered sol. only by being transformed into H_2PO_4 without passing through $Ca(H_2PO_4)_2$, which is practically insol. in H_3PO_4 (at least if not in strong excess). Complete soln. of (1) coincides with the appearance of an acid reaction to methyl orange. Addition of acid to (2) gives an immediate acid reaction with methyl orange. For $Ca_4(PO_4)_2$ the possibility of the forms (1) $|Ca|Ca|Ca|(PO_4)_2$,

(2) $|Ca|Ca|(PO_4)_2$, (3) $|Ca|Ca|(PO_4)_2$ and (4) $|Ca|Ca|(PO_4)_2$ may be considered. (1) would

be a form gradually transformable by the addition of strong acid into dicalcium phosphate, then monocalcium phosphate and finally H_2PO_4 ; (2) a form passing to the above crystd. type of dicalcium phosphate and then at once to H_2PO_4 without passing through the monophosphate; (3) would pass from the triphosphate to the monophosphate without passing through the diphosphate; (4) would pass directly to H_2PO_4 , neither di- nor monophosphate being obtainable. Q. has shown that Li_4PO_4 (which is insol.) exists in 2 forms, one of the type (3) which cannot be transformed into Li_2HPO_4 but passes even with a deficiency of acid to LiH_2PO_4 , the other of the type (1) or (2) which is converted into sol. Li_2HPO_4 with a single equiv. of acid. The first is obtained by pptn. of a Li_2HPO_4 soln. with heat, the second by pptn. of the same soln. with alc. Types (1) and (3) (collectively called type (α)) of the Ca salts are transformable into monocalcium phosphate; types (2) and (4) (collectively called type (β)) are not transformable into monocalcium phosphate but are rendered sol. only by displacement of the H_3PO_4 . Pptd.

$\text{Ca}_3(\text{HPO}_4)_2$ belongs to type (α) while the phosphorites are mixts. in variable proportions of types (α) and (β) according to their source. A simple method for an approx. detn. of the quantities of these respective types (α) and (β) is proposed. 100 cc. 0.5% H_3PO_4 is added to 1 g. samples of the finely ground phosphates in well closed containers, agitated at intervals for 24 hrs. at 15° – 18° and filtered. A second series of expts. with 2% H_3PO_4 is similarly made and a third series in which the 2% H_3PO_4 acts a week or more till a state of equil. is approx. reached (when the sol. H_3PO_4 no longer sensibly increases). The quantity of H_3PO_4 is then detd. in the filtrates. The following samples were examd.: (1) Phosphorite from the Somme (35.3% P_2O_5); (2) phosphorite from Africa (38% P_2O_5); (3) Florida rock phosphate (32% P_2O_5); (4) soft Florida phosphate (29% P_2O_5); (5) phosphorite of unknown source (30%); (6) tetraphosphate—1918—(28.5% P_2O_5); (7) tetraphosphate—1919—(26.5% P_2O_5); (8) bone meal (25% P_2O_5); (9) Thomas slag (16% P_2O_5); (10) Ca metaphosphate obtained by heating mono-Ca phosphate, (11) pptd. tri-Ca phosphate, with the results:

	There is dissolved 0.5% after 24 hrs.	There is dissolved 2% after 24 hrs.	There is dissolved 2% after a week.
(1).....	20% of total P_2O_5	33% of total P_2O_5	42% of total P_2O_5
(2).....	12	21	28
(3).....	35	50	65
(4).....	50	65	75
(5).....	30	50	75
(6).....	30	45	58
(7).....	20	32	39
(8).....	70	81	84
(9).....	30	30	52
(10).....	Trace	Trace	Trace
(11).....	Completely dissolved in a few hours.		

The 2% soln. is not in such excess as to attack sensibly type (β). The quantities unattacked, that is not transformable into mono-Ca phosphate, which can be calcd. from the figures of the last column, are of the same order of size as the quantities of free H_3PO_4 in mineral superphosphates (which is never less than $1/3$ of that sol. in H_2O and often reaches $2/3$). The presence of free acid in superphosphates has been proved by Q. by means of its catalytic action on saccharose (*Stas. sper. agrar. ital.* 38, 502(1905)). Its presence is an indirect proof that there is in the phosphorites phosphate of type (β) which cannot be transformed into mono-Ca phosphate and can only be rendered sol. by displacement of the H_3PO_4 itself. Its amt. can even exceed the amt. present as mono-Ca phosphate. The free acid in bone superphosphate is, however, much less evidently, because the tri-Ca phosphate of bone meal approaches more nearly the pptd. type (α). It is presumable that phosphorites (4) and (5) containing 75% of their tri-Ca phosphate as of type (α) (transformable into mono-Ca phosphate) would have a better effect when used directly in field expts. than phosphorite (2) which contains only 28% of the (α) type. In comparing tetraphosphate with rock phosphate it should be used in comparison only with the particular phosphorite from which it was made. It would not do, for example, to compare tetraphosphate made from (4) and (5) with (2) in such expts. It does not appear from the foregoing data that the treatment to which the phosphorites are subjected in the manufacture of tetraphosphate transforms the β -phosphates into α -phosphates or increases the α -phosphates to a sensible degree.

ALBERT R. MERZ

Use of carbon dioxide as an agricultural fertilizer. ALBERT RANC. *Industrie chimique* 7, 349–51(1920).—The assimilation of C from atmospheric CO_2 proceeds most favorably when the CO_2 content of the air is 5–10% by vol., which is about 100–200 times greater than the amt. naturally present. Expts. begun in 1912 by H. Fischer

(A. Gehring, *Zentrall. K ndung Ind.* **24**, 145(1919)) on the artificial increase of the CO_2 content of air as a fertilizer gave favorable results. Large-scale expts. were conducted using blast-furnace gases which had been used either under boilers or in internal-combustion engines (Frederic Riedel, *C. A.* **14**, 2359). Hot-house expts. with tomatoes gave 175%, with potatoes 300%, with radishes 40-54% increase in yield over the control; while outside expts. gave increases of 150% for spinach, 50% for beets, 180% for potatoes, 174% for lupine, 190% for dried lupine, and 100% for barley. Riedel's expts. have shown that an increase in the assimilation of C results in an increase in the utilization of the ordinary fertilizers.

A. P.-C.

Electrochemical method for producing diphosphate from domestic raw materials. WILLHELM PALMAER. *Kgl. Landbruks-Akad. Handlr. Tid.* **59**, 291-330(1920).—P. describes the method perfected and used by him for producing di-phosphates from apatite-bearing by-products of the mines and smelters. Expts. show that the citrate-sol. portion from phosphates made according to this method has as much fertilizing value as the citrate-sol. portion from acid phosphate and Thomas phosphate.

C. O. SWANSON

Nitrogenous manures in New Zealand. Proposed utilization of the West Coast sounds for their manufacture. E. PARRY. *New Zealand J. Sci. Tech.* **3**, 129-38(1920).

—A general discussion of conditions in New Zealand.

F. M. SCHERTZ

Fumigation of citrus trees with hydrocyanic acid: Conditions influencing injury. R. S. WOGLUM. *Bur. Entomology, U. S. Dept. Agr., Bull.* **907**, 1-43(1920); cf. *C. A.* **14**, 3746.—The prefumigation and postfumigation environments of fumigated plants have to be considered as well as that during the actual treatment. Sunshine is the chief prefumigation factor that increases injury and the influence is greater at high temps. than at low. The environment after fumigation approximates in importance that during the actual treatment, both sunshine and temp. being factors in modifying the degree of injury. The optimum environment for safety to plants is diffused light or darkness at uniform temps. below 80° F. before, during and after the fumigation. By proper regulation of the dosage and length of exposure sunshine fumigation can be conducted with safety. Fumigation at temps. above 80° F. is safest under cool prefumigation and postfumigation environments. Trees in a wet soil tend to be more severely injured than healthy trees in a dry soil. Moisture on citrus trees does not increase the degree of injury.

W. H. ROSS

Toxicity of barium carbonate to rats. ERICH W. SCHWARTZ. *Bur. Chem., U. S. Dept. Agr., Bull.* **915**, 1-11(1920).—The lethal dose of crystd. BaCl_2 for rats, administered subcutaneously, is from 45 to 89 mg. per kg.; and, by stomach tube, from 350 to 535 mg. per kg. The corresponding value for BaCO_3 , *per os*, is from 630 to 750 mg. per kg. On the basis of the Ba content, the carbonate is about $\frac{2}{3}$ as active as the chloride *per os*. The av. intake of food both poisoned and unpoisoned by hungry white rats used in these tests was 1/100 of their body wt. 20% of BaCO_3 in the rat bait was found to be an efficient concn. With this percentage a rat is required to eat only from $\frac{1}{8}$ to $\frac{3}{8}$ of a meal of av. size in order to obtain the ingestion of a lethal dose of the carbonate.

W. H. ROSS

Experiments with substances against chicken lice and the dog flea (ABBOTT) 111. Treating gas liquor to form fertilizers (Brit. pat. 153,006) 21.

Fertilizer. MOLASSINE Co. and H. C. WHALLEY. *Brit.* 152,779, July 22, 1919. In a fertilizing compd., such as is described in 14,887, 1915 (*C. A.* **11**, 862), comprizing peat mixed with some substance which liberates NH_3 to an amt. sufficient to make the mass slightly alk., CaNCN is employed as the substance for generating NH_3 . As de-

scribed in the above-mentioned patent, CaCO_3 is added to prevent acidity while the NH_3 is being generated, and phosphates and potash salts may also be added. To compensate for the absence of the chlorides and sulfates formed in the compd. described in the above-mentioned patent, K or Na chloride or sulfate, or mixts. thereof, may be added.

Insecticide and fungicide. F. W. SPERR, JR. U. S. 1,366,263, Jan. 18. A mixt. of C_6H_6 , 97-98 and CS_2 , 2-3 parts or more is employed for disinfection or as an insecticide or fungicide (dild. with H_2O when sprayed on plants).

16—THE FERMENTATION INDUSTRIES

H. S. PAINE

The determination of the concentration of hydrogen ions in wines. LUIGI CASALE. *Staz. sper. agrar. ital.* 52, 375-88(1919).—Mathematical. ALBERT R. MERZ

The influence of various circumstances on the degree of plastering reached by wines. ARTURO BORNTREGER. *Staz. sper. agrar. ital.* 52, 349-60(1919).—The effect of the total pomace on the quant. result of plastering is large, increasing the sulfates (expressed as K_2SO_4) from 0.321 to 0.484% in the case of the Rosa grape and from 0.396 to 0.598% for the Catalanesca. The effect of the stems alone is very little. Increase of temp. increased the degree of plastering up to a certain point. Plastering is finished rather quickly, being accomplished within 48 hrs. at $21.5-24.5^\circ$ in small tests if shaken frequently. The formation of alc. decreases the initial sulfate content through pptn. of the gypsum simply dissolved in the must. ALBERT R. MERZ

Utilization of *Sorghum halepense* (PANTANELLI) 12. Zymase and alcoholic fermentation (GIAJA) 11A.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Radium from a pharmaceutical point of view. VICTOR RENNEBOOG. *J. pharm. Belg.* 2, 1029-34(1920).—A review dealing with the prepn., properties, and medicinal uses of Ra salts. A. G. DUMERZ

Matriculation sheets. A. SCHAMMELHOUT. *J. pharm. Belg.* 3, 26, 42, 60(1921).—Tentative monographs proposed for introduction into the Belgian National Formulary are submitted for the following items: *Coumarin*, CHCl_3 for anesthesia, and *quinine valerianate*. A. G. DUMERZ

A contribution to the study of specialties. WALTER DULIÈRE. *J. pharm. Belg.* 3, 33-34(1921).—"Gynaline," a powder labelled "for external use," consists of $\text{Na}_2\text{B}_4\text{O}_7$ 11.02 g., alum 4.52 g., NaHCO_3 83.50 g., insol. matter 0.96 g. A. G. DUMERZ

Variation statistic as auxiliary science of pharmacognosy. L. ROSENTHALER. *Ber. pharm. Ges.* 30, 392-7(1920); cf. *C. A.* 14, 2838.—A study has been made of the comparative wt. of the seeds and the alkaloidal content of *Areca nuts* and *Calabar beans* with the result that the lightest seeds have in general been found to contain a max. of alkaloid. The results of many detns. are presented in tabulated form. W. O. E.

Digitalis flowers. P. NORTHER. Univ. Freiburg. *Ber. pharm. Ges.* 30, 402-5(1920).—An examn. of this product with respect to its glucosidal activity shows it to contain 0.7% H_2O -sol. glucoside, the aq. soln. being quite stable toward heat and age. W. O. E.

The characters and composition of the oil of "*Gilletiella congolona*." A. BOULAY. *Bull. sci. pharmacol.* 27, 626-8(1920).—The oil of "*Gilletiella congolona*" is amber yellow, limpid, and has a fresh odor like that of sweet almonds. About 51 g. of oil were obtained from 100 g. of material. The Et_2O ext. is clear, but after a few days deposits crystals. The oil has a sp. gr. at 16° of 0.9159. The free acid in terms of oleic acid is 0.79%. The sapon. number is 182.5; the I_2 number, 93.8; insol. acids, 90%; sol. acids, 0.14%; sol. volatile acids, 0.77%; insol. volatile acids, 0.77%; acetyl index, 7.0%; and unsaponifiable residue about 1.14%. The fatty acids have a fusion point of 29° . Sepn. of the acids gave a group of solid members, melting at $51-52^\circ$, and having a mol. wt. of around 310. Bromination gave a deriv. melting at $41-42^\circ$, which leads B. to consider that erucic acid is a component of the mixt. Palmitic, linolenic and oleic acids are also probably present.

F. S. HAMMETT

Iodine chloride. E. FOURNEAU AND E. DONARD. *Bull. sci. pharmacol.* 27, 629-34(1920).—The solns. of ICl as normally used in medicine are composed of a mixt. of I_2 , HIO_3 , and HCl and can only be efficacious at the moment of prepn. ICl_3 does not exist in the aq. soln., but is immediately converted into HIO_3 and ICl , of which only the latter is useful. The stability of the ICl can be maintained by adding a certain amt. of sea salt to the soln. In order to obtain ICl as pure as possible and for max. utility, the best procedure consists in slowly adding the HCl to a soln. of KI in Javel water. When an atom of Cl is added to a suspension of an atom of I_2 in H_2O so as to form ICl , a portion of the I_2 remains insol. and tends to the formation of HIO_3 , but when HCl is added the I_2 dissolves instantly. In the presence of sea salt the liberation of I_2 at the expense of ICl does not occur.

F. S. HAMMETT

Platycodon as a substitute for senega root. Y. SHIMIZU. *Kensei Igaku* 5, 60 (1917); *Jap. Med. Literature* 5, 39(1920).—The root of *Platycodon grandiflorum* contains a readily sol., relatively non-toxic saponin, and is more efficacious than senega in the treatment of coughs.

JOSEPH S. HEPBURN

Thymol and carvacrol problems. D. C. L. SHERK. *Am. J. Pharm.* 93, 8-18 (1921).—The results with ether bear out the conclusions of previous workers. Thymol is completely and somewhat readily removed from a dil. alk. soln. with ether, and after 3 extns. with about equal vols. of ether, practically no thymol remains in soln. Apparently in every case it was recovered as the free phenol and readily obtained cryst. Heptane is the most indifferent solvent chemically and exts. the least amt. of thymol. This is in accord with the observations previously made that it exhibits a striking selective solvent action in many cases. It would be very valuable in purifying an alk. soln. obtained in extg. thymol from an oil. Thymol recovered by the use of CS_2 seemed to be the brightest and of the most pleasing appearance. There is some color developed in the alkali and CS_2 reacts with the dil. alkali because H_2S is given off on acidification for recovery of thymol. However, benzene is about equally effective as a solvent. The increasing concn. of alkali with diminution of thymol content does not seem to affect ether, and benzene and CS_2 respond slowly, but heptane and CCl_4 are affected very considerably. This fact is also of interest in the assay of phenol-containing oils by means of dil. alkali where heptane is used to prevent the formation of emulsions and permit easier and quicker reading of the vol. remaining unabsorbed.

W. G. GAESSLER

The production of synthetic drugs. F. HOFMANN. *Z. angew. Chem.* 33, I, 273-7 (1920).—A general address. The circumstances which led to the discovery of phenacetin, antipyrine, veronal, isopral and other synthetic prepn. are discussed. H.'s extensive experience in this line leads him to conclude that the connection between chem. structure and physiol. action of substances has been exaggerated. Under H.'s direction 600 prepn. are synthesized yearly, and when 3 of these (about 0.5%) prove of any value,

the effort is considered well spent. H. tells briefly of the origin and progress of his work on the active principle in chaunmoogra oil, which gives promise of a cure for leprosy.

S. MONODUS

Camphor production and its extraction from the leaves of the camphor tree. ANON. *Rev. prod. chim.* 23, 665-6(1920).—Statistics of production for 1912-8 are given. Expts. were carried out at Debra Dun, Ceylon, by Simonsen and Prosad Ghose to det. the feasibility of extg. camphor and camphor oil from young leaves of *Cinnamomum camphora* by steam distn. Leaves from various sources, of various ages and gathered at various seasons yielded 0.25-2.0% camphor and 0.32-4.24% oil, and branches 0.19-61% camphor oil. Figures are given for the yields from various parts of the same tree (leaves, twigs, small branches, large branches, trunk, roots) for trees of various ages (17 yrs., 22 yrs., unknown). The compn. of the camphor oil from the various parts of the trees is briefly discussed. The extn. of camphor and camphor oil from the leaves can be successfully carried out on a com. scale provided they can be collected at sufficiently low cost.

A. P.-C.

The industry of volatile citrus oils. H. C. HOLTZ. Turin. *Chem. Weekblad* 17, 674-8(1920).—The production of various citrus oils in Italy and Sicily is described. Bergamot oil is derived from certain species of *Aurantioae* and not from rue as has been stated (*Chem. Weekblad* 17, 324(1920)).

JULIAN F. SMITH

Peru balsam and its adulteration. L. VAN ITALLIE. Univ. Leyden. *Pharm. Weekblad* 57, 1383-5(1920).—A sample of Peru balsam conformed to the requirements suggested by van I. (*C. A.* 13, 3276), but was found to be adulterated with α -C₆H₇(CO₂Me)₂. Another common adulterant is Bz₂O. Both give with resorcinol and H₂SO₄ a pronounced fluorescence, while pure Peru balsam responds only very faintly to the test. The Dieterich H₂SO₄ color test (*C. A.* 3, 2843) also serves to distinguish the genuine from the adulterated balsams, which are commonly marketed as "synthetic Peru balsam." These qual. tests are particularly useful in cases of adulteration with Bz₂O, which gives the balsam nearly the same acid no. and sapon. no. as the genuine.

JULIAN F. SMITH

The pharmacy of formaldehyde, hexamethylenetetramine and the preparations made therefrom. D. VAN OS. *Pharm. Weekblad* 57, 1406-12(1920).—Author's abstract from his dissertation. For CH₂O-soap solns. the 2 best oils are olive oil and oleic acid. The best reagent for detecting and estg. C₆H₁₁N₄ (A) is picric acid. Esbach's reagent, which contains picric acid, is not applicable in presence of albumin since the picric acid ppt. is difficult to distinguish from pptd. albumin. New compds. of A with oxalic and citric acids, Me₂SO₄, veronal, saccharin, phenylquinolinecarboxylic and dicarboxylic acids (atophan and hexophan) were prepd. Only the last 2 have therapeutic value; they dissolve uric acid and urates, and aid in eliminating these substances, to a greater degree than free A. Combination in all the above cases occurred readily, in the mol. ratio 1:1. The products were, therefore, acid salts. With strong polybasic acids neutral salts are formed if A is present in excess. Very weak acids, and esters and metallic salts (from weak bases) of strong acids, combine with A; esters of weak acids, and metallic salts of strong bases, do not. As a nitrogenous, monoacidic base which forms sol. salts not extd. from aq. soln. by org. solvents, A may be considered a synthetic alkaloid. It forms no compd. and gives no ppt. with alkaloids and their salts, except that it slowly ppts. morphine from an aq. soln. of morphine-HCl. With salts of other alkaloids an equil. occurs: A + quinine-HCl \rightleftharpoons quinine + A-HCl. When given internally, very little A reaches the bladder unchanged unless it is protected from the stomach acidity, e. g., by use of hard gelatin capsules. The same is true of its salts. The harmful effect of A on pepsin activity in the body (Howell and Keyser, *C. A.* 11, 2388) is much lessened in its compds. with boric and citric acids

(borovertin and helmitole), but much increased in its compds. with salicylic and sulfo-salicylic acids. Doubt still exists as to the value of hard gelatin capsules in administering A. The gastric juice diffuses into the capsule and liberates CH_4O from A, thus greatly hardening the inner wall of the capsule. The resulting stress between the inner and outer walls may even burst the capsule while still in the stomach.

JULIAN F. SMITH

Protection of medicines against the action of light. J. B. M. COEBERGH. *Pharm. Weekblad* 57, 1452-7(1920).—Compds. listed in the Holland Pharm. IV as requiring protection from light were subjected to various wave lengths of light, obtained by filtering sunlight through solns. of quinine- H_2SO_4 and of CuSO_4 at different concns. EtBr , FeCl_3 , NH_4Cl , FeCl_3 soln., Na-Fe pyrophosphate soln., Hg-NH_4 chloride soln., CHCl_3 (containing EtOH), KI and NaI were not affected by light. Other compds. may be grouped according to the wave lengths of light to which they are sensitive: (a) up to 408μ : HBr , HNO_3 , monobromocamphor, quinine and its salts, dimethylaminoantipyrine, CHI_3 , physostigmine- H_2SO_4 , mercurous tannate; (b) 408 - 450μ : Et_2O , HgCl_2 , santonin; (c) 450 - 500μ : Cl water; (d) 500 - 550μ : $\text{Fe}_2(\text{P}_2\text{O}_7)_3$ with NH_4 citrate; (e) 550 - 600μ : BzOH , Ag proteinate, HgI_2 , resorcin, β -naphthol, pyrogallol; (f) 600 - 700μ : apomorphine- HCl , HgI_2 , PhOH ; (g) below 450 and above 600μ : CHBr_3 , sweet spirit of niter; (h) below 500 and above 600μ : H_2O_2 soln.; (i) above 600μ : HCN , tincture of I; (k) all wave lengths: HgO , P, liquefied PhOH , adrenaline- HCl soln. Varieties of glass and their light-transmitting properties are: dark red (Cu_2O) glass transmits rays above 700μ ; dark brown (C and S) glass, above 500μ (light brown transmits even the ultraviolet rays); thick dark green (FeO), above 450μ ; light yellow-green (Cr_2O_3 - CuO), above 450μ ; dark yellow-green, 470 - 660μ ; blue glass, red, ultraviolet, violet and blue rays; black (not opaque) glass, red, ultraviolet and violet. The best kinds of glass for protecting the above groups of medicines are: (a) red, brown and green; (b) red, dark brown or green; (c) red or dark brown; (d) and (e) red; (f) to (k) should be kept in the dark. To protect these during light exposure necessary to use, red glass is best for groups (f) and (k), and dark green for (g), (h) and (i). To test brown or green glass for group (a), fill with a 1% soln. of benzidine in CHCl_3 and expose to bright sunlight for 5.5 hrs. The soln. should show no turbidity. To test dark brown, green or red glass, expose celloidin paper in the bottles to violet or ultraviolet light for 80 min. The paper should show no discoloration. J. F. S.

Study of the pharmacy of opium. H. DE ILAAN. *Dissertation*, Amsterdam (1920); *Pharm. Weekblad* 57, 1483-5(1920).—In the detn. of meconic acid in opium by van der Wielen's 1910 method, much better results are obtained by extg. with 0.1 N HCl instead of with H_2O . The picrate method is suitable for the sepn. of morphine and narceine, but is not applicable to a Ca(OH)_2 ext. of opium. The oxalate method is suitable for sepg. narcotine from papaverine, but not for the quant. detn. of papaverine. In making an ext. or tincture of opium, the yield is improved by acidifying the H_2O or EtOH to 0.1 N with HCl . Domestic culture of opium (in Holland) is not feasible, chiefly on account of the high labor cost and low yield of alkaloids. J. F. S.

Composition of Mothersill's Sea-Sick-Cure. H. L. VISSER. Nijmegen. *Pharm. Weekblad* 57, 1578(1920).—Capsules of Mothersill's Sea-Sick-Cure are reported (*Secret Remedies* and Martindale's *Extra Pharmacopoeia*) as containing chloretone, caffeine, and stearin, but no monobromocamphor. Analyses of authentic samples showed the presence of monobromocamphor and the absence of chloretone. The brown capsules contain cinnamon. Both kinds contain caffeine. These analyses also revealed the presence of considerable amts. of atropine in both the red and the brown capsules. This dangerous constituent has not been reported in previous analyses of the remedy.

JULIAN F. SMITH

A test for benzoic acid based on diazotization; applied to toxicological testing for atropine, cocaine and stovaine. MARCET, GUERBERT. *J. pharm. chim.* 22, 331-3(1920).—To 0.1 mg. or more of BzOH or alkaloid yielding it, add 3-4 drops of fuming HNO_3 (d. 1.49), evap., take up the mixed *o*-, *m*-, *p*- (NO_2) compds. with 1 drop of a 10% SnCl_2 soln., heat for 2-3 min., cool and add 2 drops of a 1% NaNO_2 soln. and 3-4 drops of a 1% β -naphthol soln. in 10% NH_4OH . A deep orange-red ppt. is formed. The dried ppt. dissolves in 1 cc. of concd. H_2SO_4 to a violet-red; the soln. poured into H_2O produces brilliant orange-yellow, still visible with 0.01 mg. of BzOH. S. W.

Ergot, its history and chemistry. GEORGE BARGER. *Pharm. J.* 105, 470-3 (1920); cf. Tschirch, C. A. 11, 2531; Gordon Sharp, *Pharm. J.* 85, 3968(1910).—A critical history of ergot is given in all its phases, including ergotism, etiology, and medicinal properties. The present chem. knowledge of ergot is summarized as follows: The chief active principles are: (a) the amorphous alkaloid *ergotoxine*, $\text{C}_{28}\text{H}_{40}\text{O}_4\text{N}_2$ (B. Carr and Ewins, C. A. 1, 584, 1508, 1711; 4, 1612), identical with *hydroergotinine* of Kraft (C. A. 1, 82; 2, 2972) and with Tanret's amorphous *ergotinine*; Dale (cf. C. A. 1, 1996) produced gangrene with it, (b) *histamine (ergamine)*, $\text{C}_8\text{H}_9\text{N}$ (B. C. A. 4, 2182; 5, 2109); a powerful, uterine stimulant, (c) *tyramine*, $\text{C}_8\text{H}_9\text{ON}$ (B., C. A. 3, 2727, 2807; 4, 1018), the chief blood pressure raising principle of the fluidext., (d) *acetylcholine*, $\text{C}_8\text{H}_{17}\text{O}_2\text{N}$ (Ewins, C. A. 8, 3078) lowers the blood pressure, is present in variable, small amts. (e) several inert substances peculiar to ergot: (1) The cryst. alkaloid *ergotinine* $\text{C}_{28}\text{H}_{40}\text{O}_4\text{N}_2$ of Tanret (1875), the anhydride of (a), both interconvertible; (2) *ergothioneine*, $\text{C}_{28}\text{H}_{40}\text{O}_4\text{N}_2\cdot 2\text{H}_2\text{O}$ (Tanret, C. A. 3, 2679; 4, 763; B. and Ewins, C. A. 6, 1154); (3) *secale aminosulfonic acid*, $\text{C}_{28}\text{H}_{40}\text{O}_4\text{N}_2\text{SO}_3\text{H}$, cryst., H_2O -sol. (Kraft, loc. cit.); (4) *secalonic acid* (Kraft), $\text{C}_{28}\text{H}_{40}\text{O}_4$, a cryst. yellow coloring matter, m. 244°; (5) another yellow substance, $\text{C}_{28}\text{H}_{40}\text{O}_4\cdot \text{H}_2\text{O}$, m. 350° (Freeborn, C. A. 6, 2287); (6) *sclererythrin*, the characteristic red coloring matter (Dragendorff and Podwissotski, 1877); (7) *Clavicepsin*, $\text{C}_{28}\text{H}_{40}\text{O}_4$, a glucoside (Marino-Zucco and Pasquero, C. A. 6, 410); (8) *ergosterol* and *fungisterol* (Tanret, C. A. 2, 3058; 3, 423). Finally, substances of general occurrence are present, viz.: (a) 30-33% of fat (Rathje, C. A. 3, 961); (b) free amino acids, e. g., *leucine*, *isoleucine*, *valine* (Van Slyke, C. A. 3, 2587; 4, 2350); probably *aspartic acid* (B. and Dale, C. A. 1, 1996); (c) amines derived from amino acids by loss of CO_2H , e. g., *histamine* and *tyramine*; hence these are not derived from ergotinine and *ergotoxine*, as stated by Tschirch. Much less active are (d) *putrescine* and *cadaverine* (Rieländer, *Sitz. Ges. Naturf. Marburg*, 1908; cf. C. A. 2, 2817, 1293; 9, 3099); also *isoamylamine* (B. and Dale, C. A. 4, 596) and *agmatine* (Engeland and Kutscher, C. A. 4, 3248); (e) *choline* in ergot is the source of NMe₃ (B., *Z. physiol. Chem.* 11, 184 (1887)); (f) *betaine* and *uracil* were found by Rieländer, betaine also by Kraft; (g) *vermine* $\text{C}_{28}\text{H}_{40}\text{O}_4\text{N}_2\cdot 3\text{H}_2\text{O}$ (Schulze and Bosshard, *Z. physiol. Chem.* 10, 80(1887)) occurs also in leguminous seedlings. Finally, ergot contains *lactic acid*, *mannitol*, and the disaccharide *trehalose*. S. WALDBOTT

Uzara; what is it? H. G. GREENISH. *Pharm. J.* 105, 474-5(1920).—This remedy for dysentery and diarrhoea in the African lake district was discovered in that region by H. W. A. Hopf, in a plant of *Asclepiadaceae*. Chem. and physiol. exams. were made by O. Hinz (C. A. 8, 374, 2428), A. Gürber and E. Frey (C. A. 8, 3471). A specimen received from the (German) authorities, was identified as *Dicoma anomala*, Sonder, of *Compositae*; it is used by the Kaffirs in colic (cf. following abstract). S. WALDBOTT

Note on Uzara. E. M. HOLMES. *Pharm. J.* 105, 507(1920).—From available descriptions of the plant (cf. preceding abstract), H. traces the origin of uzara to *Schizoglossum Shirens*, N. E. Brown, *Asclepiadaceae*, and recommends importation of the root of this plant into England for chem. examn. S. WALDBOTT

The content of ammonium salts in various opiums. JAMES LESLIE THOMSON. *Pharm. J.* 105, 550(1920).—In the opium assay by the Brit. Pharm. method, the odor

of NH_3 is noted. In 71 samples of opium, T. set free the NH_3 from its meconic, lactic and H_2SO_4 salts by boiling with Na_2CO_3 , absorbed it in excess of 0.1 N HCl, and titrated back with 0.1 N Ba(OH) $_2$ (methyl red). The av. amt. of NH_3 in 21 Turkish samples was 0.22% (0.09-0.47); in 48 Indian, 0.21% (0.17-0.27); in 2 Persian opiums 0.18% (0.15-0.21). Possibly the NH_3 may be formed in the drying of the juice. If it is present in the fresh latex, it would no doubt have an important function in the synthesis of the alkaloids, *e. g.*, by action on aldehydes, forming amino-alcs., capable of ring formation. (Robinson.) In discussion, D. B. Dott refers to licorice as another NH_3 -bearing plant.

S. WALDBOTT

The assaying of opium. ARTHUR J. JONES. *Pharm. J.* 105, 550-2(1920).—A criticism of D. B. Dott's modification of the official Brit. Pharm. process (*C. A.* 14, 2869). In discussion, D. upholds his method, while declaring that the assay of opium does not admit of scientific accuracy. The acceptance of a *uniform*, standard method for both buyer and seller is needed.

S. WALDBOTT

A new source of santonin. HENRY G. GREENISH AND CONSTANCE E. PEARSON. *Pharm. J.* 106, 2-3(1921).—Leaves of a species of *Artemisia* from N. India were identified as being derived from *A. brevifolia*, Wallich. Upon extn. by Fromme's method (H. Engelhardt and L. E. O'Brian, *Drug. Cir.*, 1913, 443; *Yearbook Pharm.*, 1914, 138; cf. *C. A.* 6, 3311), 1% of santonin was found. Exams. are in prepn. to det. in which part of the plant and at what period the highest % of santonin occurs. S. W.

Note on commercial formaldehyde. GEORGE F. MERSON. *Pharm. J.* 106, 4(1921).—Com. lots of HCHO received from the U. S., usually contain HCHO 88% and MeOH 14%. In a recent lot, MeOH was entirely replaced by 13 + % of EtOH (proof spirit), no doubt for economic reasons.

S. WALDBOTT

Note on tinctura iodi (French Codex). GEORGE WALKER. *Pharm. J.* 106, 4-5(1921).—This tincture, containing 1 g. I in 9 g. of 95% EtOH; or approx. 40 grains per fluidounce, has been used by Louis Bordreau (*J. méd. Bordeaux*, Jan. 1914), in his large-dose I treatment of tuberculosis, and again by T. Bird (*Lancet*, March 6, 1920, 546). If alc. of the Brit. Pharm. (90%) is used in the same ratio, not all of the I will dissolve. W. suggests formulas to bring about complete soln. by adding abs. EtOH, Et $_2$ O, or a small amt. of KI. To obtain exactness in giving fluid doses, W. detd. the following solubilities of I in alcs. of varying strength, in terms of, resp., wt. in wt., wt. in vol. and grains in minims: Abs. alc., resp., 1:6.00, 1:7.60, 1:8.34; 95% alc., 1:6.58, 1:8.07, 1:8.90; 90% alc., 1:10.50, 1:12.59, 1:13.90. Notable deviations from these results occur in various pharmacopeias, except the Dutch.

S. WALDBOTT

An incompatible chloral mixture. JOSEPH TAIT. *Pharm. J.* 106, 5-6(1921).—A certain prescription contained: Chloral hydrate, 2 drachms; tinct. nucis vom., 3; tinct. belladonna, 1; KBr, 4; liq. opii sed., 2.5 drachms; tinct. hyoscyam., 1 ounce; spirit ammon. aromat., 2; and aq. menth. pip., 6 ounces. Several reactions are liable to occur: (1) Liberation of CHCl_3 by NH_4OH and by $(\text{NH}_4)_2\text{CO}_3$, in the latter case, CO_2 is also given off. Sep. expts. show that the CHCl_3 is held in soln. by the EtOH present; but warning to 65° seps. it; (2) liberation of strychnine; EtOH holds it in soln.; but if CHCl_3 seps. it, carries the alkaloid with it, and the bottom doses become dangerous; (3) possible sepn. of an oily layer of chloral alcoholate upon long standing or at low temp. (cf. Ruddiman, *Incompatibilities*); (4) the above mixt. causes a bulky resinous ppt., due to tinct. of hyoscyamus when dild. The prescription was filled by dispensing the spirit of NH_3 in a sep. bottle.

S. WALDBOTT

Adulterated neocarsphenamine and identity reactions. P. BOHNY AND P. FLEISSIG. *Schweiz. A. polh.-Ztg.* 58, 521-4(1920).—A sample, contg. no As, consisted of 33% NaCl, 66% sand, and was colored yellow with ochr. Four similar cases on record are quoted. Cf. *C. A.* 13, 990; 14, 3125; 15, 144.

S. WALDBOTT

Argentum proteinicum, albumose silvæ, protein silvar, protargol. LUDWIG KNÖRR. Munich. *Schweiz. Apoth.-Ztg.* 58, 597-603(1920); cf. *C. A.* 7, 1074.—Present com. samples contain the full amt. of Ag, but show a defective mode of its combination with org. substance, the latter being at times of doubtful character (gelatin, etc.). K. recommends for the next German Pharm.: (1) Detn. of Ag by the Marchner-Rupp method (*C. A.* 7, 210, 1401), using the original, not pre-dried substance, and requiring a minimum of 7.78% Ag; (2) loss by drying not to exceed 3%; (3) a test for the absence of NH_3 ; (4) clear soly.; (5) identity tests: To 5 cc. of a 2% soln. add HCl drop by drop; the ppt., on further addition of 15 cc. of 25% HCl in the cold, redissolves. Shake 1.0 g. of albumose-Ag with 10 cc. abs. EtOH for 3 min., filter; the filtrate (about 7 cc.), filled up to 10 cc. with HCl, must not turn turbid. This method detects 0.1-0.2% of ionic Ag salts.

S. WALDBOTT

Felamin, a new gallstone remedy. ANON. *Schweiz. Apoth.-Ztg.* 58, 628-9(1920).—This combination of $(\text{CH}_3)_4\text{N}_4$ with the active principle of oxgall is white or faintly greenish, hygroscopic, bitterish sweet, sol. in H_2O with alk. reaction; sol. in EtOH; insol. in benzine. In the form of sugar tablets, each has 0.3 g. of the active substance. With dil. H_2SO_4 the aq. soln. of felamin turns milky, then ppts. white. To test for felamin, suspend 0.2 g. of this ppt. in 1 cc. H_2O , then add $\frac{1}{2}$ of its vol. of concd. H_2SO_4 , keeping the temp. below 60° ; shake and add a trace of furfural; the liquid turns carmine red.

S. WALDBOTT

Proposed vegetable drug deletions. A. R. BLISS, JR. *J. Am. Pharm. Assoc.* 9, 767-71(1920).—At one time the U. S. Pharmacopeia was a book for physicians and a guide to the medicinal agents prescribed by them. Of late the work has become a book of standards for manufacturers. A questionnaire was sent to 513 physicians in Atlanta asking which of the 121 vegetable drugs now official should be deleted from the U. S. P. IX. Replies were received from 387. Only 30 drugs received unanimous vote for retention. Over 50% of the physicians advised deletion of 31 other drugs, although no drug received a unanimous vote for deletion. Only a few votes advised deletion of any drug described in Useful Drugs. So far as the evidence goes it shows that many of the official vegetable drugs are considered inert, useless, worthless, obsolete, of limited utility or of questionable value.

L. E. WARREN

Suggestions for improvement of U. S. P. processes. FRANTZ F. BERO. *J. Am. Pharm. Assoc.* 9, 772-5(1920).—In the assay of the fluidexts. of *ipeacac* and *cinchona* it is recommended to use purified asbestos instead of oak sawdust, as the former may be found in every lab., while the latter is often difficult to obtain. The addition of 10-15 cc. of H_2O to cause balling is not necessary as in the old method. The evapn. should be made below 80° since *ipeacac* alkaloids are prone to decompose if the temp. becomes high. *Cocaine hydrochloride*. The U. S. P. gives no purity rubric or assay method. The m. p. of $183-9^\circ$ given by the U. S. P. has been disputed, some chemists claiming the value is near 200° . An assay process should be included, either by titration of the HCl or by shaking out the alkaloid. *Cresol*. The U. S. P. states that this substance is sol. in 50 vols. of H_2O . The trade article requires more than 50 and only in rare instances is a sample found which is sol. in 100 of H_2O . Likewise the statement that 1 cc. of cresol should be sol. in 60 cc. of H_2O without more than a slight turbidity is incorrect. *Compound cresol soln.* Since the Insecticide Act requires a statement of the amt. of inert ingredients (generally H_2O), an assay process should be included. *Methanol*. The test for MeOH in EtOH is not satisfactory, the reason being that the fuchsin on the market is apt to be unreliable. *Copaiba*. The U. S. P. states that a hard, brittle residue should be left on evapn. of the volatile oil. B. finds that some genuine specimens give a semi-solid mass. The test for *Gurjun balsam* is not reliable since pure specimens sometimes respond to the test. *Oleoresin of aspidium*. Specimens assay from 8

to 26% of filicin by the method of the Swiss Pharmacopeia. Some standard should be adopted. *Opium*. A Gooch or an alundum crucible for collecting the morphine crystals is recommended in place of a pledget of cotton. L. E. WARREN

Assay of aromatic sulfuric acid. E. F. KILLEY AND J. C. KRANTZ, JR. *J. Am. Pharm. Assoc.* 9, 775-6(1920).—The U. S. P. assay is often criticized and other methods have been suggested, none of which are satisfactory. A new method gives excellent results. Weigh about 5 cc. of the specimen into a beaker, add 30 cc. of *N* NaOH and evap. to dryness on a sand bath. Dissolve the residue in 20 cc. of H_2O and titrate the excess of alkali with H_2SO_4 using methyl orange as indicator. Phenolphthalein is not a satisfactory indicator since the alkaline mixt. absorbs CO_2 while being evapd.

L. E. WARREN

Commercial hydrastis. ARNO VIEHÖVER. *J. Am. Pharm. Assoc.* 9, 779-84 (1920).—Authentic samples of domestic hydrastis were collected in different states in 1917 and 1918. The specimens were examd. for H_2O , alkaloid, total ash and acid-insol. ash. The rhizomes and rootlets were studied separately. The rhizomes are richer in alkaloid than the rootlets. Nearly all of the specimens of rhizomes exceeded the minimum limit of the U. S. P. for alkaloids (2.5%). It is still undecided whether the drug should be collected in the spring or in the autumn. The ash in nearly all of the samples was high. This was due in most cases to adhering dirt, which it is almost impossible to wash off if it is allowed to dry on after the drug is collected. An ash content of 8% is suggested, together with 3% of acid-insol. ash. If properly cleaned, the drug is almost sure to run below 8% in ash and over 2.75% in alkaloids.

L. E. WARREN

The solubility of volatile oils in mixtures of alcohol and water. H. C. WOOD. *J. Am. Pharm. Assoc.* 9, 878-81(1920).—An approximate method for the detn. of the soly. of volatile oils in EtOH. A known vol. of oil is dissolved in a known vol. of 93% EtOH and H_2O is added from a buret until the appearance of a faint, permanent ppt. The amts. of EtOH and of oil are readily calcd. from the data. Corrections for the shrinkage in vol. of mixts. of EtOH and H_2O are given, which must be applied. L. E. WARREN

Experiences in the manufacture and standardization of Dakin's solution. A. J. SELLS. *J. Am. Pharm. Assoc.* 9, 881-3(1920).—The formula for making Dakin's soln. as formerly used by the A. E. F. in France did not give a satisfactory product. Sells' modification proved satisfactory. Dissolve 140 g. of Na_2CO_3 in 8 l. of H_2O , add 20 g. of $CaCl_2O_2$ (25% available Cl_2), agitate thoroughly, allow to stand 30 min., filter and assay for NaOCl in the usual way. Dil. to the required strength and add H_3BO_3 in small amts. until the mixt. is neutral to phenolphthalein, the latter being added in an aq. suspension. To the neutral soln. 2 g. of H_3BO_3 are added per l. L. E. W.

A new formaldehyde soap (CRONER) 27. Food and drug legislation (MCCRAE) 12.

Gehes Codex der Bezeichnungen von Arzneimitteln, kosmetischen Präparaten und wichtigen technischen Produkten mit kurzen Bemerkungen über Zusammensetzung Anwendung und Dosierung, sowie einer Verdeutschung der vorkommenden fremdsprachlichen Fachausdrücke. 3rd Ed. Dresden: Gehe & Co., A. G. 680 pp. For review see *Pharm. Weekblad* 58, 103(1921).

Medicinal composition for treating syphilis. W. M. HABEEB. U. S. 1,365,241, Jan. 11. A medicinal compn. of spongy appearance, consisting of metallic Hg, $CuSO_4$ and vegetable material such as cypress nuts or cones, henna, nut gall and pomegranate peel is employed for fumigation treatment of syphilis.

Germicide. C. A. WEEKS. U. S. 1,366,106, Jan. 18. An oily germicide adapted for use on wounds is formed of a dichloro deriv. of eucalyptus oil mixed with vehicles such as paraffin oil, alc., ether or ointment bases.

Alkaloids. CHEMISCHE FABRIK VORM. SANDOZ. Brit. 153,219, Aug. 16, 1919. Addition to 125,396 (C. A. 13, 2256). Alkaloids are selectively isolated from drugs containing more than one constituent by taking advantage of their varying basicities and their different solubilities in various solvents. The raw alkaloidal material containing more than one constituent, mixed if necessary with powdered vegetable tissue, is acidified and treated with a suitable solvent, whereby the weakly basic alkaloids are extd., leaving the strongly basic alkaloids fixed in the tissue. Further vegetable tissue is then added to the concd. ext. and the weakly basic alkaloids are fixed thereto by the addition of acid. Both vegetable residues are then separately treated according to the methods described in the principal patent and in 134,197 (C. A. 14, 799). By a choice of solvent, one alkaloid can be extd. from all the remainder. The isolation of morphine from opium and the sepn. of the remaining alkaloids into weakly and strongly basic components are described in the example. Alkaloids of the narcotic group comprise the weakly basic components.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

T. LYNTON BRIGGS

The Dawson sulfuric acid plant. H. ROYAL DAWSON. *Chem. Age* (London) 4, 15(1921).—In order to save land space and at the same time secure the obtain in the normal allowance of chamber space per lb. of S, that is made possible by placing towers between the chambers, the "towers" or barriers are placed within the chambers, two to a chamber. The mixed gases pass horizontally through these barriers, which are as wide and as high as the interior of the chamber. Cool chamber acid, with some additional water at times, trickles down through the barriers from a reservoir at the top of the chamber. Diagrams of the arrangement are given.

C. C. VANVOORHIS

Graphic calculation of neutralization of caustic liquors with carbon dioxide. JOSEPH C. DITTMER. *Chem. Met. Eng.* 23, 1179(1920).—A sample method of calcn. which the av. process-man can work is explained and illustrated by graph and problems. The 3 factors involved are the amts. of CO₂, caustic liquor and NaOH content of the caustic.

W. C. EBAUGH

The industrial preparation of alkali cyanides from the dry-distillation products of vinasse. F. SCHÖNFELD. *Chem. Listy* 14, 192-5(1920).—The vinasse is concd. to 40° Bé. containing about 4% of N. The compn. of the N compds. fluctuates; therefore, results such as obtained by Lajbl (C. A. 15, 293), are not of great value. The vinasse preheated to 100° enters the kiln chambers and is there subjected to dry distn. The org. N compds., especially betaine, form amines, mostly Me₃N. At 1000° the Me₃N thus formed decomposes and forms among other products HCN. The heat of the gaseous mixt., resulting from the dry distn., is utilized for preheating the incoming vinasse. At this point the removal from the gases of the amorphous C and ashes present is accomplished and the temp. reduced to 110°. The gases are then led through condensers, where their temp. is lowered to 50-60°. The condensed water formed contains some NH₃, amines, NH₄CN, and free HCN. This water is used to dil. the H₂SO₄ in the absorbing vats. The resulting (NH₄)₂SO₄ soln. is concd. and the crystals are sepd. by centrifugals. The final product contains about 20% N. The gases, after passing the H₂SO₄ soln., are further cooled in absorption towers. At 8° absorption by water is complete and a 2-3% HCN soln. is obtained. This is then distd. under reduced pressure and the HCN reabsorbed in dil. NaOH soln., which is then concd.

in vacuo and centrifuged. The dried salt is ground and formed into 400-g. briquets. The mixt. of gases, after the HCN has been extd., contains CO, CH₄, H, N, C₂H₂, O, CO₂, and as it has a calorific value of 3500, is used for firing the kilns. 36 kg. of C, 20 kg. of tar, about 6.7 kg. of NaCN and 4-4.5 kg. of (NH₄)₂SO₄ are obtained from 100 kg. of vinasse. The remaining cyanides in the residual waters from the process are recovered in the form of Paris blue.

JOHN M. KENO

The utilization of marine algae. PAUL GLOSS. *Mon. sci.* 10, 217-21(1920); cf. *C. A.* 14, 1859.—The French army used demineralized sea weeds as a feed for horses and found it a satisfactory substitute for oats. I, Br and K were recovered commercially. The weeds were dried in the air, placed in open ditches and fired. The ash thus obtained was fused and transported to factories where KCl was leached out and I and Br were displaced by Cl₂. The residual char was sold for fertilizer. The disadvantages of the process are loss of heat, dependency upon weather conditions for drying, and the volatilization of some I and Br caused by the high temp. of fusing. In a newer process patented by the writer in March 1919 the fresh weeds are dried and incinerated in a furnace with a special grate consisting of inclined steps. The weeds are forced down the grate while a counter current of heated gases hastens their drying. In this process one kg. of weeds yields 3500 to 4000 cal. Also, since it is not necessary to fuse the ash, the salts are more easily washed out and I and Br are not lost by volatilization.

S. D. KIRKPATRICK

Diatomaceous earth. NORRIS GOODWIN. *Chem. Met. Eng.* 23, 1158-60(1920).—A resumé of the history, occurrence, properties and uses of diatomaceous earth, accompanied by an extensive bibliography.

W. C. EBAUGH

Hydrogen. GEORGES CARTERET. *L'âge de fer* 36, 738-41(1920).—General review of methods of prepn. and of a few of its properties and industrial applications.

A. P.-C.

Titanium—its method of preparation and industrial applications. GEORGES CARTERET. *L'âge de fer* 36, 670-2(1920).—A brief review of the methods and localities of occurrence of Ti ores, of its history, prepn., and use (for incandescent lamp filaments), of its compds. and their uses (for bleaching textiles, white and colored pigments, porcelain enamel, artificial teeth, tanning), and of the G. Carteret and M. Devaux process for the prepn. of TiO₂, which is as follows: The finely pulverized ore is reduced at a red heat with coal in the presence of a flux and then treated with dry Cl₂ gas. The 2 operations may be carried out simultaneously by using a reducing gas mixed with Cl₂. The various chlorides (Fe, Si, Ti, etc.), are formed successively as the temp. increases, and are subsequently sepd. by fractional distn. The aq. TiCl₄ soln. is treated with alkali carbonate, and the gelatinous TiO₂ thus obtained is exceptionally pure. On boiling in a bath slightly acidified with H₂SO₄ it passes to a dense unctuous mass, which is particularly suited for use as a pigment.

A. P.-C.

Equilibrium of the system water and the chlorides and sulfates of sodium and magnesium at 105° (MAVEDA) 2. The ammonia-soda process (WILLIAMS) 6.

Production of nitric acid. K. B. QUINAN. *Can.* 208,370, Feb. 8, 1921. Gases containing oxides of N are repeatedly brought into contact with water or dil. HNO₃ by distributing the latter over permeable diaphragms through which the gases are caused to pass. Cf. *C. A.* 14, 97.

Chamber plant for manufacture of sulfuric acid. J. H. BROWN. U. S. 1,365,964, Jan. 18. The plant is provided with a burner and app. for successively washing and reheating the burner gases prior to oxidation.

Ammonia from cyanamides. W. O. SNELLING. U. S. 1,365,739, Jan. 18. In prepg. NH_3 by the reaction of H_2O upon a cyanamide, a cold suspension of the cyanamide in H_2O is brought into heat-interchanging relation with hot reaction products derived from cyanamide suspension previously supplied to the reaction app.

Ammonia; catalysts. NORSK HYDRO-ELEKTRISK KVAELSTOFKARTISSELSKAB. Brit. 153,290, Sept. 27, 1920. Catalysts for use in the synthesis of NH_3 are prepd. by heating, preferably to a temp. below 500° in a neutral atm., simple cyanides of the metals, Fe, Ni, Co and Cr, or complex cyanides of such metals, not containing a cyanide of alkali or alk. earth metal, or in which the mol. proportion of such cyanide to the heavy metal cyanide is less than 2.1; by the use of these catalysts the synthesis of NH_3 can be carried out at a temp. below 400° and while using a pressure less than 100 atms. Suitable initial compds. are ferrous cyanide, ferrocyanic acid, $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$, triammonium potassium ferrocyanide, potassium ferrous ferrocyanide (Everitts' salts), potassium ferric ferro cyanide (Williamson's violet). It is advantageous to add to initial materials not containing alkali or alk. earth metals, a proportion of a compd. of such metal, KNO_3 , *e. g.*, but the relative proportions above indicated must not be exceeded.

Ammonia; catalysts. SOC. L'AIR LIQUIDE (SOC. ANON. POUR L'ETUDE ET L'EXPLOITATION DES PROCÉDÉS G. CLAUDE). Brit. 153,254, Oct. 21, 1920. A catalytic material, for use in the synthetic manuf. of NH_3 under high pressure, consists of an oxide of Fe approximating in compn. to Fe_3O_4 , prepd. by directing a jet of O on molten FeO. A small quantity of lime may preferably be incorporated in the product. A bar of Fe or steel is fused under a jet of O and the molten product, which consists of FeO mixed with Fe, is collected in a crucible, preferably of MgO. 5–10% of CaO may be added at this stage, together with a small amt. of alkali oxides. The jet of O is then directed upon the molten mass, whereby large quantities of heat are evolved, the mass becomes agitated, and the CaO is dissolved in the oxidized melt, as well as some of the MgO of the crucible. The treatment is continued until the mass is completely homogeneous, or if impurities are present, until the surface begins to congeal, when the product is cast on a sheet of Fe. Cf. 130,086 (C. A. 14, 104).

Ammonium sulfate. G. N. VIS. U. S. 1,368,301, Jan. 18. NH_3 is absorbed from gases by NaHSO_4 free from uncombined H_2SO_4 to produce a double sulfate and the latter is decomposed by dilg. and refrigerating the soln. to cause deposition of cryst. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

Ammonium sulfate. G. N. VIS. U. S. 1,368,302, Jan. 18. NH_3 is absorbed from other gases or from steam by the action of NaHSO_4 in the presence of H_2O (at a temp. of about 70°) insufficient to dissolve the NaHSO_4 . The resulting double sulfate and liquid are heated to about 111° to decompose the double sulfate, solid Na_2SO_4 is sepd. and $(\text{NH}_4)_2\text{SO}_4$ is then recovered from the liquid portion.

Recovery of ammonia from gases. G. N. VIS. U. S. 1,368,303, Jan. 18. NH_3 is absorbed from other gases or steam by the action of NaHSO_4 to produce a double sulfate and the latter is heated to a temp. of 350 – 600° to liberate NH_3 and regenerate NaHSO_4 for further use in the process.

Ammonium sulfate. C. BOSCH. Can. 208,833, Feb. 22, 1921. CaSO_4 is treated with $(\text{NH}_4)_2\text{CO}_3$ in the presence of water, the soln. is filtered with a dipped hollow frame filter and the layers of carbonate are washed free from $(\text{NH}_4)_2\text{SO}_4$.

Ammonium sulfate. R. LESSING. Brit. 152,766, July 21, 1919. The coloring matter usually associated with crystals of $(\text{NH}_4)_2\text{SO}_4$ is removed by agitating the latter, in a detached condition in a clear satd. soln. of that salt, maintained slightly acid—if necessary by the addition of H_2SO_4 —and floating of the suspended impurities. The agitation may be performed mechanically, or by blowing with air or steam but pref-

erably it is effected by means of the satd. $(\text{NH}_4)_2\text{SO}_4$ soln., which enters at a point near the bottom of the conical treatment vessel containing the crystals. The rapid stream on entering stirs up the crystals, but as the diam. of the vessel increases only the impurities remain suspended. A suitable app. is specified.

Thorium nitrate. H. N. MCCOY. U. S. 1,366,128, Jan. 18. Monazite sand is heated with concd. H_2SO_4 for several hrs. to produce an insol. Th compd., sol. impurities are sepd., and the residue is then recovered as a filter-cake mud and boiled with NaOH soln. to obtain Th hydroxide, from which other Th compds. may then be made.

Zirconium salts. H. WADZ. Brit. 153,113, Aug. 8, 1919. A new basic sulfate of Zr of the compn. $5\text{ZrO}_2 \cdot 3\text{SO}_4 \cdot 13\text{H}_2\text{O}$ free from Fe, Ti, and Si is obtained by adding H_2SO_4 in the requisite quantity to a soln. of Zr oxychloride containing free acid, preferably HCl . The basic sulfate is pptd. on heating.

Sodium pentaborate; boric acid. SCHORR & GEN. Brit. 153,007, Oct. 11, 1920. Boro natro calcite is treated with H_2O or mother-liquor and enough H_2SO_4 to form CaSO_4 but without giving the mixt. an acid reaction and the mixt. is heated to 75° and filtered. The filtrate is concd. and cooled to obtain $\text{Na}_2\text{O} \cdot 0.5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$; some H_3BO_3 remains in soln. and may be recovered. The residue consists of CaSO_4 and unchanged boro-natrocalcite. It is treated with H_2O or mother-liquor and enough H_2SO_4 to make the mixt. acid, and is then filtered. CaSO_4 remains on the filter, and H_3BO_3 is recovered from the filtrate.

Zinc chloride from scruff. G. H. CLEGG. U. S. 1,365,456, Jan. 11. Scruff formed in tinning pots in the manuf. of tin andterne plates is crushed and agitated with cold H_2O and lighter particles of sludge are sepd. from the ZnCl_2 in the liquor in order to recover the latter. *Palmitin and palmitic acid* are distd. from the sludge.

Hydrogen. C. TONIOLO and DR. ROSSI OFFICINE ELETTROCHIMICHE. Brit. 152,975, Dec. 24, 1919. H or mixts. of N and H are obtained by treating with steam and preferably in the presence of a catalyst the gases from elec. and blast smelting-furnaces, and subsequently eliminating the steam, CO and CO_2 ; H is obtained if the gases treated are those from elec. smelting-furnaces or from blast furnaces fed with O; in other cases, a mixt. of N and H is obtained, the relative proportions of the two constituents depending on whether the furnace is blown with air or air enriched with O. The H obtained from elec. furnace, etc., gases may be mixed with the poorer mixt. from blast-furnace gases, or with N; also, this poorer mixt. may be mixed with H. The gases after reaction with steam are passed through H_2O scrubbers to remove the excess of steam, and then treated with alkali or alkaline earth substances or with H_2O under pressure to remove CO_2 ; traces of CO and CO_2 are removed by NaOH , Cu salts, etc. When suitably purified, the gases may be used in the hydrogenation of fats, the synthesis of NH_3 , as fuel for internal-combustion engines, and for welding.

Hydrogen. G. F. JAUBERT. U. S. 1,366,185, Jan. 18. Powdered ferro-Si is given a preliminary treatment with H_2O to decompose the phosphides which it contains and form a pasty mass and the material thus purified is then used for reaction with a caustic alkali soln. to produce H. Cf. C. A. 14, 3766.

Purifying hydrogen. J. HARGER and H. TERREY. U. S. 1,366,176, Jan. 18. A gas containing H and CO is caused to react with O in the presence of a catalyst such as oxides of Fe, Bi and Ce at a temp. (preferably about 150 – 250°), such as will effect selective oxidation of the CO to CO_2 without material oxidation of the H and the CO_2 formed is sepd. from the H.

Sulfur. FARBENFABRIKEN VORM. F. BAYER & Co. Brit. 153,297, Oct. 15, 1920. S is obtained from H_2S , or from gases such as illuminating gas which contain

H_2S , by mixing with air or O and bringing the mixt. into contact with porous C obtained in the manner described in German specification 290,656. The reaction does not require any external heat. The S is pptd. upon the C in the fused state or as flowers of S , and is removed by sublimation or by extrn. with a solvent. In gases having a small H_2S content, the oxidation is accelerated by the addition of small quantities of NH_3 or an amine. Cf. *C. A.* 14, 3508.

Sulfur. H. C. PEDERSEN. Brit. 152,887, Dec. 10, 1919. S is extd. from Fe pyrites and other sulfide ores by roasting with a limited supply of air in the presence of solid carbonaceous material in quantity sufficient to effect complete reduction within the charge of the SO_2 produced during roasting, but insufficient to effect the reduction of the ore to metal. The process may be carried out in an ordinary pyrite-roasting furnace, or in a shaft furnace provided at the bottom with tuyères, the amt. of air introduced being adjusted to the height of the charge column and to the compn. of the charge.

Sulfur from sulfur ores. N. E. KATZ. U. S. 1,365,922, Jan. 18. S ore is heated with H_2O in an autoclave to a temp. sufficient to melt the S by the steam generated.

Separating nickel from cobalt. M. J. UOY and O. C. RALSTON. U. S. 1,365,358, Jan. 11. Co is pptd. from Co-Ni solns. by simultaneously subjecting the soln. to the action of Cl and CaCO_3 at a temp. of about $0-4^\circ$, which is below the temp. at which a material pptn. of Ni occurs.

Treatment of zinc solutions. ELIAS F. PETERSSON. Can. 208,600, Feb. 15, 1921. Sol. silica is recovered from Zn solns. for electrolysis by treating the solns. with an excess of an alk. earth carbonate at $90-100^\circ$.

Purification of zinc solutions. F. PETERSSON and METALS EXTRACTION CORPORATION. Brit. 152,752, July 17, 1919. In the purification of Zn solns., and in particular the prepn. of Zn solns. for electrolysis, SiO_2 is deposited in a filterable form by adding an alkali or alk. earth carbonate in slight excess to the neutral or substantially neutral liquor at an elevated temp. In an example, a ground ZnS ore is roasted to convert to oxide and sulfate and then after re-grinding is added to hot H_2SO_4 of 10-15% strength, which may be that obtained from the electrolytic cells. When the acidity has been reduced to 5% it is still further diminished to 1% by the addition of a mixed ppt. of ZnO , ZnCO_3 and Fe_2O_3 , obtained in a subsequent stage in the purification. Neutralization is finally attained by adding whiting in the form of powder or of a milk made with H_2O . The SiO_2 is then pptd. by adding about 10 lbs. of whiting per ton of liquor and maintaining the temp. at $90-100^\circ$ for a short time with agitation. After filtration, the SiO_2 is washed with H_2O to free it from Zn . It is desirable to neutralize as much of the H_2SO_4 as possible with Zn , as in the example, and in the method described in 104,897, but the neutralization may be effected by the addition of whiting only.

Treating zinc. ELECTROLYTIC ZINC CO. OF AUSTRALASIA PROPRIETARY. Brit. 152,997, Oct. 23, 1920. Finely divided Zn or Zn dust for use in the purification of Zn solns. prior to electrolysis, for pptg. metals from cyanide or other solns., and as a reducing agent in the prepn. of org. compds., is treated with a view to increasing its activity. The Zn may be stirred with boiling H_2O or with a soln. of an alkali such as NaOH .

Aluminothermic production of zinc and corundum. KOHLER und ERZ G. m. b. H. Ger. 319,814, May 8, 1917. An intimate mixt. of Al , ZnO of a high degree of purity, and Zn dust is subjected to the aluminothermic process. The Zn dust is added in such amt. that the speed of the reaction is regulated, and the excess heat of the reaction is utilized. The Zn vapor may be condensed, and the Al_2O_3 obtained as a high-grade corundum. The excess heat is used to melt down the otherwise difficultly melted Zn dust.

Removing copper from the bore of ordnance. A. E. A. DAGORY. U. S. 1,366,187, Jan. 18. Cu deposits in the bore of guns are removed by firing an alloy of Sn 55 and Pb 45% through the gun. Cf. C. A. 15, 361.

Jewelry. K. MURAKAMI. Brit. 152,914, Feb. 11, 1920. The eye lenses of fish or sea animals are boiled in H₂O until solid, and the white coating of gelatinous matter is removed by a soln. of NaOH. The hard cryst. lens so obtained is transparent, and is washed with H₂O and polished with NaCl or Na₂SO₄. These lenses may be prevented from breaking by a long immersion in formalin. They can be stored without damage by coating them with wax or gum. The gelatinous matter removed may be recovered and used for *glue-making*. The lenses are converted into imitation pearls by the pptn. of insol. white metallic salts within their substance, and into artificial gems by pptg. colored salts, or by using a dye. The gems are rendered lustrous by a coating of equal parts of collodion and ether.

Composition for making a leather substitute. W. W. CARTER. U. S. 1,365,891, Jan. 18. A material adapted for insulating or use as a substitute for leather is prepd. by mixing an alkali xanthate soln. with a hemp or Manila paper stock or similar org. filling material and alk. soln. of copal or shellac or similar substance and then neutralizing with NaHSO₃.

Composite plates for electrical insulation or similar uses. J. R. McCLAIN. U. S. 1,365,330, Jan. 11. Sheets of fibrous material such as muslin, duck or paper are impregnated with a shellac soln. or a similar binder, several sheets are superposed to form a plate and this is subjected to heat and pressure to compact it and harden the binder. The plate is then divided into the several layers of which it is composed and a layer of the material thus prepd. is placed upon the upper and lower surfaces of a plate formed of fibrous material such as other paper or cloth sheets impregnated with shellac or a similar binder and the article thus formed is heated and pressed to unite its component parts and render it suitable for use as a smooth-surfaced elec. insulation.

Plastic material containing zein. C. E. SWETT. U. S. 1,365,607, Jan. 11. A compn. adapted for stiffening shoe blank fabrics is formed of zein mixed with rosin and phenol. The mixt. may also be used for the manuf. of molded articles. Cf. C. A. 14, 3167.

Heat-resisting cement. H. S. ASHENHURST. U. S. 1,365,077, Jan. 11. A heat-resisting cement adapted for use on hot Fe or steel is formed of finely divided asbestos 95.5, a water-sol. salt such as a nitrate or chloride 4.5 parts and H₂O. Among the salts which may be used are NaNO₃, KNO₃, NH₄NO₃, K₂SO₄, Na₂SO₄, (NH₄)₂SO₄, NaCl, NH₄Cl, CaCl₂ and SrCl₂.

Plastic compositions. C. F. CURTIS. Brit. 153,089, July 29, 1919. A compn. made by melting the solid residue of coal-tar distn. after all separately valuable constituents have been removed with an approx. equal vol. of coal-tar pitch, and adding a smaller quantity of an absorptive granular substance, such as sawdust, with or without a small proportion of short-fibred asbestos is suitable for roofing, and the like. In an example, 7 parts by wt. of residue are melted and 5 parts of tar are stirred in, 0.3 part by wt. of wood dust are gradually added, and, if desired, 1 part of asbestos. The compn. may be poured over the surface and trowelled, or it may be run out in sheet form and stored.

Vesicular materials and compositions. C. W. BOYNTON. Brit. 153,030, Apr. 16, 1919. A cellular product which is of low apparent sp. gr., a non-conductor of heat and electricity, free from laminations, and substantially impervious to H₂O is obtained by reducing clay or shale to a uniformly fine condition, and treating it in a dry, plastic, or slurry state under gradually increasing temp. until the mass softens and swells owing to the generation of gas from some of its constituents. A suitable clay contains SiO₂

49 parts, Al_2O_3 21 parts, Fe_2O_3 11 parts, C 2 parts, and negligible quantities of CaO and MgO. Generally, the clay or shale should be rich in metallic oxides, compds. of C, S, Na, K, or the like, the nature and proportions of flux and gas-generating ingredients being preferably such that the material softens at the same temp. as the gas is generated. Additions or subtractions may be made to ensure this. Excess of Fe, CaO and MgO should be avoided. The material is ground and may be used dry, or as slurry, or it may be made into a plastic mass and molded, in which case it is advisable to preheat the articles to drive off superfluous H_2O . The temp. of burning varies; it may be as low as 1040° . If the product is to be used for insulation or as an aggregate for concrete, oxidation of the surface during burning should be avoided. The product may be preformed into slabs, tiles, or the like or crushed and added to cement. The invention is distinguished from those in which clays, shales, slates, and the like, are heated to produce porous masses.

Compositions for floor coverings, balls, etc. P. R. LANG. Brit. 152,869, Oct. 28, 1919. Materials for floor coverings, artificial cork, wood, etc., are placed in perforated molds and are heated in a vacuum chamber. The materials comprise a filler of ground cork, ground wood, fiber, asbestos, etc., mixed with casein and powdered glue and one of the phenol-HCHO condensation products or synthetics of the same. A suitable construction is specified.

Elastic masses for insulating, billiard balls, etc. BAYER & CO. Ger. 309,224, Dec. 11, 1917. "Methylene ketone" or its homologs and analogs, is subjected to polymerization. E. g., "methylene ethyl methyl ketone" is allowed to stand for several weeks at a temp. of 30° . The product is solid, colorless, hard, firm and elastic, and takes a polish readily.

Coating with copper. J. D. SMITH. Brit. 152,835, Sept. 5, 1919. A Cu-salt soln. is reduced by hydrazine hydrate in the presence of NH_3 , the Cu being deposited as a coherent coating on heated, non-conducting, smooth or polished surfaces, such as glass, china, porcelain, and the like, in contact with the soln. The coating liquid can be prepd. by adding strong CuSO_4 soln. to a strong soln. of hydrazine sulfate in hot H_2O until a faint blue color persists on standing and a pale-blue powder is pptd. If not for immediate use, the powder may be filtered and dried. When used, it is suspended in cold H_2O , a few drops of cold hydrazine sulfate soln. added, followed slowly by a soln. of NH_3 until the liquid turns dark brown, when NaOH soln. is added until a slight yellow or orange ppt. persists after shaking. The ppt. is dissolved by a little hydrazine sulfate, yielding the clear yellowish or brownish liquid required.

Stereotype molds. A. W. SPERLING. U. S. 1,366,032, Jan. 18. A sheet for making stereotype molds is formed by satg. blotting paper with a soln. of Na silicate, removing surplus soln. by pressure and then pressing the sheet against a sheet of blotting paper which contains glycerol to transfer a film of glycerol to the first mentioned sheet. Sheets thus prepd. are adapted for receiving impressions of typewriter type for directly making a stereotype mold.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

British chemical glass industry. S. N. JENKINSON. *Chem. Age* (London) 3, 619(1920).—The leading British chem. glasses are compared with Jena glass, for resistance to action of boiling HCl and HCl vapor. For figures see C. A. 12, 212.

DONALD E. SHARP

The devitrification of glass, a surface phenomenon. The repair of crystallized

glass apparatus. ALBERT F. O. GERMANN. *J. Am. Chem. Soc.* 43, 11-4(1921).—The silicates composing a glass are in equil. with a surface film of moisture, and are more or less hydrolyzed so that H_2SiO_3 , $\text{Ca}(\text{OH})_2$ and NaOH may be present. The bases absorb CO_2 from the air and become hydrogen carbonates. Heating expels adsorbed moisture, dehydrating the H_2SiO_3 and roughening the surface. Old or devitrified glass may be worked over a lamp by first washing with HF . This may be taken advantage of in repairing old app.

DONALD E. SHARP

Shock-defying glass. ANON. *Mining and Metallurgy* No. 169, 50 pp.(1921).—Laminated glass is made in various thicknesses to withstand almost any impact to which glass might be subjected. Glass for bank tellers' cages is made of three thicknesses of glass. The middle section is plate glass nearly $\frac{3}{16}$ in. thick; the two outer parts are $\frac{1}{8}$ in. thick. Between the core and the outer sheets are imposed sheets of transparent pyroxylin 0.2 in. thick. A piece of glass of this compn., 6 in. square, was shot at from a distance of 3 ft., with a rifle using a 32-caliber, nickel-jacket, flat nose, high-velocity rifle bullet. The bullet powdered the glass at the point of impact over an area $1\frac{1}{2}$ in. in diam. The bullet, however, penetrated only the top layer of the glass and the sheeting was exposed only in one spot about $\frac{3}{8}$ in. in diam., but it was not even dented by the bullet. The heavy plate-glass core was broken as was the under-sheet of glass, but was not penetrated and the only glass that fell from the underside of the block were some pieces so small that they could have caused no injury had they fallen on a person even from a great height. Glass for windows liable to be subjected to shock from explosions need only be the thickness of two ordinary sheets of window glass with one sheet of the pyroxylin sheeting between them. The lamination is effected by hydraulic pressure. If an explosion causes the glass to crack, it is prevented from falling by the pyroxylin core.

CHARLES E. MUNROE

The decoration of porcelain. H. BANARD. *Pottery Gaz.* 46, 85-91(1921).—True oriental porcelain is fired only sufficiently in the first firing to permit handling and the hard firing takes place during the glost firing. General decorative processes are described.

H. G. S.

Acid clay and acid soil (KOBAYASHI) 15. Acidity of Japanese acid clay (KOBAYASHI) 15.

Glass. M. A. SMITH. U. S. 1,365,797, Jan. 18. A glass having a low coeff. of expansion and high resistance to temp. changes is formed from silica 60, B_2O_3 10, Al_2O_3 7, NaNO_3 9, Na_2CO_3 10, CaCO_3 3, and As_2O_3 1 part.

White clouded glass, enamels or glazes. E. RIETZ. U. S. 1,366,101, Jan. 18. White clouded glass, enamel or glaze is prepd. by the use of unpurified clouding material such as natural compds. of Zr, together with sufficient material containing F, e. g., Na_2SiF_6 , to prevent discoloring of the product. A batch may be formed of quartz 20, feldspar 35, soda 10, MgCO_3 5, crude ZrO_2 10 and Na_2SiF_6 20 parts. Cf. C. A. 15, 299.

Glass; artificial stone. P. B. CROSSLEY. Brit. 152,780, July 22, 1919. Non-fragile glass, which can be rolled, forged, extruded, cast, etc., is made by dissolving in the dry state such silicates as micaceous or asbestos minerals in molten glass or similar silicate. The glass, etc., is chosen so as to melt at a temp. below the temp. at which the mica, etc., effloresce. If the product is to be machined, an excess of mica, etc., should be present over the amt. required to form a satd. soln.

Preparing glass, china and like surfaces for varnish. F. MEYER. Ger. 319,744, July 8, 1919. Addition to 317,656 (C. A. 15, 183). The glass, china or like surface is roughened by means of H_2F_2 .

Crucible melting furnace. C. M. SRIN. U. S. 1,365,204, Jan. 11. The furnace is of the regenerator type and is adapted for the melting of glass.

Refractory material. L. DENIS. U. S. 1,365,230, Jan. 11. A porous refractory material adapted for use in surface combustion furnaces is formed of 30 parts of a pure rich refractory earth such as contains less than 80% of sand, 25 parts of a poor earth such as light sandy soil, 30% of magnesia, and 5 of sawdust. In the prepn. of the material the sawdust is burned out to produce a porous product.

Furnace lining. J. F. MOLLEN and W. W. PATNOR. U. S. 1,356,336, Jan. 11. A material adapted for lining furnaces is prepd. by making a slurry of raw dolomite, adding a small % of NaCl and then passing the mixt. through a rotary kiln operated at a temp. sufficiently high to calcine the dolomite and volatilize the NaCl. The presence of the NaCl serves to maintain the material in granular form.

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

The action of chemicals on concrete. M. JACOBSON AND J. G. DE KÉRAVENANT. *Industrie chimique* 7, 391(1920).—Brief review of the action of acids, acid salts, alkalies and alk. salts, coal-tar derivs., fertilizers, oils and fats on concrete. A. P.-C.

Treatment of piles with salt on New Orleans Great Northern. H. VON SCHRECK. *Ry. Maint. Engr.* 16, 462(1920).—In March 1913 shallow boxes were built around the heads of piles immediately under the cap and the boxes filled with rock salt. The salt boxes were given attention irregularly, av. filling being once each year. Recent inspection develops that the treated piling is in splendid shape while the untreated piling is badly decayed and will have to be renewed during the coming year.

R. C. B.

Paving compositions. A. R. ALEXANDER. Brit. 152,857, Oct. 10, 1919. Sand, soil, stone, clay, or other finely divided earthy matter is mixed, preferably *in vacuo*, with a mineral asphaltic binder, other than tar, which has been previously treated under heat with sol. mineral salts, other than chlorides, such as sulfates or selenates of Al, Cr, Mn, Fe, Ir, Ga, Na, K, Rb, Cs, NH₄, Ag, Au, Pt, or Tl, which temper or harden the binder. The binder is employed to the extent of 8–17% of the mass. The product is used for road paving or as a base upon which the ordinary wearing course may be laid, or the foundation and wearing courses may have the same compn. and may be laid separately and connected while the compn. of one course is in a highly heated condition so that the two will be united.

Molding bricks, pipes, etc. A. O. CROZIER. Brit. 152,748, July 17, 1919. Cement and like articles, such as bricks, blocks, and pipes, are made by pouring into an upright shaft a column of cement mixt. of such a height as to effect by its own wt. a compacting of the lower part of the column, which is then cut off, or cut off and cut up, and removed; the remainder of the column then descends, and the shaft is filled up again. A suitable construction is specified.

Fibrous weather-resisting sheet adapted for roofing. W. F. MCKAY. U. S. 1,365,711, Jan. 18. A weather-proof sheet is formed of outer layers of material such as asphalted paper with an intermediate layer of overlapping strands of straw, arranged criss-cross and bonded with a bituminous compn. or similar material, all compressed together. Cf. C. A. 14, 109.

Heating and coloring wood. H. F. WEISS. U. S. 1,366,225, Jan. 18. Wood is heated in a current of air to a temp. of about 200° for a sufficient time to transform the

wood into a uniformly colored or darkened condition with reduction of its moisture-absorbing tendency.

21—FUELS, GAS, TAR AND COKE

It is with deep regret that we announce the death, on March 11th, of Mr. J. D. Pennock, who has served faithfully and well as Assistant Editor of *Chemical Abstracts* in charge of this section since the beginning of the journal in 1907. By this sudden death the Journal has sustained a great loss. It would be difficult to overestimate the value of the unselfish service which Mr. Pennock rendered during his long connection with *Chemical Abstracts*.

A graphical method for the interpretation of flue gas analysis. GILBERT B. HOWARTH. Univ. Leeds. *J. Soc. Chem. Ind.* 39, 329-33T(1920).—Lengthy calcs. are generalized by coördinate charts to show (1) the ratio of the amt. of air supplied for combustion to the minimum theoretical amt. for complete combustion, and (2) the ratio of the amt. of heat in the hot flue gases to that liberated by combustion of the fuel. Four variables are involved, of which it is necessary to know two: (1) The % extra air based on the minimum required for combustion; (2) the % O in the dry flue gases; (3) the % CO₂ in the same; (4) a const. depending on the compn. of the fuel. These 4 variables are plotted so that if the values of any 2 are known, the others are detd. The method is most useful when the constant (fuel factor) is known, so that detn. of the % CO₂ alone in the dry flue gases gives the % O and the extra air. These graphs are applicable to nearly all fuels. The value of the fuel factor from lignite to anthracite varies from 0.63 to 0.40, representing a difference of 0.5% in CO₂. The detn. of any physical property of the flue gases may be made by superimposing curves on the extra-air diagram. In this way measurements can be made on flue gases satd. with H₂O at any temp. by a series of curves. Also in *Blast Furnace & Steel Plant* 9, 175-8(1921).

C. C. DAVIS

Fuel saving by furnace efficiency. SYDNEY N. DUGUID. *Chem. Age* (London) 3, 592-3(1920).—See C. A. 14, 3778.

The use of liquid fuels in industrial furnaces, and especially under steam boilers. LOUIS CAUCHOIS. *Bull. soc. ind. Rouen* 48, 301-28(1920).—A general review of the properties of various liquid fuels (petroleum, shale oil, coal tar, C₆H₆, alc.), of the manner of, and the precautions necessary in handling and using them, and of their merits in comparison with coal.

A. P.-C.

Power from German peat. FRIEDR. BARTEL. *Elektrotechn. Z.* 41, 865(1920).—An elaborate account of a proposed 120,000-kw. power plant utilizing peat as fuel. Details of present smaller peat installations are given, including figures on the consumption of peat per kw.-hr.

C. G. F.

Lighting in theory and practice. W. E. BUSH. *Gas World* 74, 48-9(1921).—Lighting in terms of c. p. is being replaced by that in terms of lumens, which may be defined as the "quantity of light necessary to produce an av. illumination of 1 foot-candle over an area of 1 sq. ft.," or the amt. of light escaping from a hole 1 ft. square in the side of a sphere with a radius of 1 ft. lighted by a 1 c. p. light in the center. By multiplying the mean spherical c. p. of a lamp by 12.57, the number of lumens emitted by that lamp are obtained. A simple, portable app., known as a foot-candle meter, has been designed to measure lumens. (Cf. C. A. 13, 529 for such an app.) The efficiency of illumination for any given room may be detd. by the formula: Intensity in foot-candles × area in sq. ft. ÷ utilization factor. By the latter is meant the ratio

of the useful light (that is the light not absorbed by the walls, etc.) to the total light produced by the lamp. Arbitrary data have already been evolved for the useful light for any class of interior and type of fitting.

J. L. WILEY

Gas industry on the heat-unit basis. III. Distributing British thermal units. WALTER HOLB. *Gas J.* 153, 154-6(1921).—Some of the difficulties met in distributing the lower-grade gas are discussed. The present systems are overtaxed, due to the larger vol. of gas to be distributed for equal duty and its greater density. Higher pressures are necessary, putting greater strain on the distributing system and tending to increase leakage. This latter difficulty is hardly tenable owing to the fact that since the gas is of higher density, the leakage is approx. inversely proportional to the sq. root of the d. Corrosion is accelerated in mains, governors and meters and naphthalene troubles are increased owing to the denudation of the gas of its light oils. The former can be alleviated by eliminating the causes by removing the CN compds. or to some extent by spraying into the gas a certain amt. of light oils or petroleum oil. It can be accomplished also by compressing the gas to a lower pressure than is required for distribution and then expanding it in suitable app., to the pressure of distribution. B. t. u. standards will also tend to eliminate the smaller sizes of mains and service pipes; the minimum size in the future for the former should be not less than 4-in., and for the latter not less than 1-in. Considerable extension in boosting systems must also be provided for out-lying districts. **High-pressure distribution of B. t. u.** B. R. PARKINSON. *Ibid.*, 156-8.—Similar to above. **IV. Heat-unit basis in relation to power supply.** DUGALD CLERK. *Ibid.*, 218-9.—In order to extend the gas industry into the power field, attention must be directed toward obtaining the lowest price per therm for power purposes, and providing an alternative supply of gas to the mfr. from a more acceptable source than a private producer plant. **Gas regulation act as it applies to the industrial load.** RALPH HALKETT. *Ibid.*, 219-20.—More economical production and lower prices per therm are necessary to a large development of business in industrial gas. Also higher thermal efficiencies are necessary in industrial appliances.

J. L. WILEY

Application of reinforced concrete to general gas-works practice. L. H. THOMAS. *Gas J.* 153, 228-30(1921).—T. discusses the use of concrete for foundations, storage bunkers and tanks, and gas mains. The best example of the latter is the Hume pipe which is made by a centrifugal process, the resulting concrete being very dense and hard. Pipes can be made to withstand 400 lbs. pressure per sq. in. without percolation.

J. L. WILEY

A simple apparatus of small capacity for production of water gas. ANON. *J. usines à gaz* 44, 369-71(1920), 2 figs.—The app. described is suitable for very small plants making not more than 10-50 cu. m. of water gas or carbureted water gas per hr., but demanding a thermal yield comparable to plants of greater capacity. This app. is composed essentially of a steel jacket lined with refractory material and containing a 3-part retort; a cylindrical part occupying the lower half; a truncated cone of smaller diam. inverted over this cylinder; and a similar but shorter cone fitting exactly upon the larger base of the first cone and serving for the mouth of the retort. The first cone functions as a continuous feeder for the retort proper. The blow period, lasting only 45 sec., is carried out alternately through tuyères leading in under the grate and into the annular space at the top of the cylinder, the air being controlled by a 3-way valve, thus working up a uniformly high temp. throughout the fuel mass without any appreciable formation of CO. Because of the height of the column of fuel, the max. amt. of CO is formed during the period of gasification lasting 4 min. Steam is admitted through the lower tuyère and oil or tar for carbureting purposes into the top of the cylinder opposite the upper tuyère. The operation which is very satisfactory, is described in detail.

J. L. WILEY

Increasing capacity of purifiers. GEO. WEHRLE. *Gas Age* 47, 41-2(1921).—The oxide capacity of the purifying boxes at the Denver Gas and Electric Light Company's plant was trebled for the same ground space by simply extending the boxes upward. Construction details are given. Since the change, the boxes last longer between changes than the difference between former and present capacity would attain, thus indicating that more gas is being purified per bushel of oxide. Revivification in place is practiced by blowing air through the oxide at stated intervals. J. L. WILEY

Steam raising on gas works. H. L. BATEMAN. *Gas World* 74, 58-60(1921); *Gas J.* 153, 161-4(1921).—A discussion is given of the conditions, type of boilers, and auxiliary equipment, for burning low-grade fuels in gas plants. Either Lancashire or water-tube boilers are satisfactory provided forced draft is used and a sufficiently large grate area is installed. A test on a B. and W. boiler with chain-grate stokers burning coke breeze with forced draft showed under the conditions given an efficiency of 78.28%. J. L. WILEY

Gasification of lignite and wood. R. GEIPERT. *J. Gasbel.* 63, 792-4(1920).—The following comparisons are made between gas-coal, lignite and wood for the purpose of showing their relative worth for gasification purposes.

	Coal 100 kg.	Lignite 100 kg.	Wood 100 kg.
Gas cu. m.....	29	16.6	27.6
Calorific value per cu. m. calories.....	5400	3300	3000
Total calorific value.....	156000	54780	82800
Coke kg.....	70	26.2	16.1
Tar kg.....	5	2	2
NH ₃ kg.....	0.34
Consumption of fuel per each 1000 gaseous calories, kg.	0.256	1.642	1.21
Relative worth calcg. all by-products at market value			
Marks.....	46.40	12.78	16.05

Therefore, if gas-coal laid down at the plant costs 30 Marks per 100 kg., lignite and wood, in order to compete as a gas-making material, would have to be delivered cost-free at the plant. Some details are given as regards the gasification of each type of fuel. (Cf. C. A. 14, 614, 1750, 3780.) J. L. WILEY

The influence of cooling the fire in a producer on the production of gas from natural fuels. HERMANN KOSCHMIEDER. Berlin-Friedenau. *Brennstoff Chem.* 2, 3-5(1921).—Calcn. of the heat balance in a producer cooled by H₂O-vapor and the influence of the latter upon vol. and calorific value of the gas produced are discussed. W. B. V.

City gas of the future. R. B. HARPER. *J. Western Soc. Eng.* 26, No. 1 (Tech. Sec.) 1-15(1921), 12 charts.—H. traces the progress of the gas industry from its earliest days to the present heat value standards. The trend now is in the direction of gasification of coal in coke ovens and the coke in water-gas plants and mixing the coal gas with the blue water gas to produce a mixed gas of about 350 B. t. u., consisting of 80-85% of blue water gas and 15-20% of coal gas. Such a gas would permit the economical use of coal and the max. production of gas therefrom on the basis of gas-making material costs. Such a gas should be very stable in quality, burn well, and when consumed in burners properly adjusted, should give good service. J. L. WILEY

Composition of coke-oven gas. P. LEBBAU AND A. DAMIENS. *Compt. rend.* 171, 1385-7(1920).—Four samples of coke-oven gas from four different kinds of coal were examd. by a method previously devised (C. A. 12, 1444) for use with retort gas. Less H, more N and CH₄ were found than with retort gas and small amts. each of C₂H₄ and C₂H₆. H. LE CHATELIER gives as the reason for this, that the penetration of air into the oven increased the N content, and the O tended to oxidize the C₂H₄ and the C₂H₆.

He advocates use of silica brick to prevent this leakage of air through the oven walls.

J. L. WILEY

Economy of utilizing peat in Swiss gas works. ZOLLIKOFER. *J. Gasbel.* 63, 755-6(1920).—The gasification of peat in gas retorts is not profitable; as a generator fuel it may be used as a substitute for coke, releasing the latter for other purposes, but generally has no economic utility in connection with gas plants. J. L. WILEY

New producer oil gas plant. F. C. BINNALL. *Gas Age* 47, 47-51(1921), 7 figs. —A description is given of a novel process for making 1000 cu. ft. of 450-B. t. u. gas without use of external retort firing and with 4 gal. of oil. The process is known as the *Dayton Process*. In principle, it is essentially an air-oil process in which air and oil are fed into hot retorts through a proportioning atomizer. Within the retorts partial combustion or combination of certain constituents of the oil takes place with the O of the air supplied, liberating sufficient heat to promote and continuously maintain the temp. for thermal decompn. of the hydrocarbons. Just enough air is admitted to the retort with the oil to liberate by this partial combustion sufficient heat to gasify the rest of the mixt. and maintain the retort temps. without the application of external heating. Approx. 88-89% of the heat units in the oil is obtained in a usable form as gas or tar. The only raw material required is a liquid hydrocarbon mixed with preheated air in predetd. and automatically maintained proportions, and fed continuously into retorts located within properly insulated settings. The grade of gas can be varied at will from 300 to 560 B. t. u. by adjusting the air-oil ratio control on the atomizer. The cost per 1000 cu. ft. of gas is 35.22 cents. The gas analyzes % by vol. CO₂ 6.1, unsatd. hydrocarbons 14.7, O₂ 0.9, CO 5.6, satd. hydrocarbons 7.8, H₂ 1.7, N₂ 63.2, total S grains per 100 cu. ft. 1 to 2. Details of construction and operation are given.

J. L. WILEY

Stenches for detecting leakage of blue water gas and natural gas. S. H. KATZ AND V. C. ALLISON. *Bur. Mines, Tech. Paper* 267, 22 pp.(1920); cf. *C. A.* 15, 281.—Impregnation of natural gas or blue water gas with a stench-imparting chemical provides a means for reducing loss from leakage and for eliminating accidental poisoning and explosions. The chemical, physical and physiological properties of several materials have been investigated and directions are given for their use. Of those examined, amyl thioether, ethyl mercaptan, phenyl isocyanide and pyridine present the best possibilities. None of these mentioned containing S carries enough of it to inhibit com. use of the gas. Savings resulting from the use of stench in gas would probably total more than the costs of the stench.

J. L. WILEY

Action of steam and gases on yields of ammonia from carbonization of oil shales and coal. ARTHUR J. FRANKS. *Chem. Met. Eng.* 23, 1149-54(1920).—A discussion of the various factors and physico-chem. laws affecting the NH₃ equil., the synthetic action of steam and H and removing action of inert gases from the decompn. zone. Facts regarding the decompn. of NH₃ are: (1) The decompn. is endothermal; increase in temp. increases decompn.; (2) decompn. gives increase in vol.; increased pressure of N₂ and H₂ decreases decompn.; (3) inert gases at const. vol. do not affect the decompn.; inert gases at const. pressure increase decompn.; (4) the concn. of H₂ is more potent than the concn. of NH₃ or N₂ in shifting the equil., for concn. of H₂ is raised to the third power in the equil. equation. In retorting at low temp. (under 500°) the concn. of NH₃ is <5% and of H₂ is 25 to 30%. The effect is to decrease decompn. In retorting at low temp. with steam, the steam acts mainly as an inert gas to sweep the NH₃ from the hot zone and forestall decompn. In retorting at high temp. (800° to 900°) concn. of H₂ in the gas is 45 to 55% which greatly hinders the decompn. Also according to Tervet (*J. Soc. Chem. Ind.* 2, 445) NH₃ is formed by the action of H₂ on the combined N of the coke. With steam at high temp. C forms CO and H₂; both the protective

action and the Tervet synthesis are increased. In addition steam acts to sweep the NH_3 from the hot zone and prevent decompn. Rate of decompn. is even more important in the explanation of the conservation of NH_3 in retorting, and this is expressed by $K[\text{NH}_3]^2 = k[\text{H}_2][\text{N}_2]$. The concn. of NH_3 is small, usually 1 or 2% with a liberal use of steam and the concn. of H_2 which is many times larger appears as the cube in the equation. The catalyzing action of the hot wall of the retort also is important, some writers even denying that the decompn. takes place at all in the gas phase. Application of the principles discussed to the explanation of the action of steam and inert gases on the NH_3 yield during carbonization leads to the general deductions that at low temp. the steam and gases act both to prevent dissociation of NH_3 by their presence and to remove it mechanically before material decompn. occurs. At high temp. steam has also a synthetic action owing to the production of large quantities of nascent H through its reaction with the hot coke and the union with some of the N contained therein to form new NH_3 . The low percentage of NH_3 and the high % of H in the gases operate to quicken the rate of combination to form NH_3 and, what is of more importance, to depress the rate of decompn., which has been shown to be very slow. Although the depressing effect of the H on the dissociation does not appear to be as great in the few cases cited as would be expected from theoretical considerations, its influence must be felt, since it is present in the gas mixt. in amts. 25 to 50 times greater than that of NH_3 . However, the very slow dissociation rate of NH_3 is the real key to F.'s exposition.

J. J. MORGAN

Discoloration of sulfate of ammonia. ANON. *Chem. Age* (London) 3, 678-80 (1920).— $(\text{NH}_4)_2\text{SO}_4$ of high quality as well as of high N content, is now demanded. A blue color is due to ferrocyanides, resulting from faulty regulation of sp. gr. in the saturator, for the color rarely appears when Twaddell is above 54°. Local alkalinity and priming must be guarded against. Yellow discolorations are due to As_2S_3 and As_2S_5 coming from the acid used, or to iron sulfates. Pink and red discolorations are caused by $\text{Fe}(\text{CNS})_3$ or phenols. Methods for combating these difficulties are suggested.

W. C. BRAUGH

The Walter Feld process (of removing ammonia and hydrogen sulfide from coal gas). F. RASCHIG. Ludwigshafen. *Z. angew. Chem.* 33, I, 260-2 (1920).—The process was proposed by Feld (*C. A.* 6, 1962) in 1912, but its installation was delayed by Feld's death in 1914 and the war. Later R. with Lepsius of Berlin and Markel of London undertook the installation at a large coke-oven plant in Oberhausen. R. studied especially the reactions based on the assumption that the gas contains 2NH_3 for each H_2S : (1a) $(\text{NH}_4)_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{S} = 2(\text{NH}_4)_2\text{S}_2\text{O}_7$; (1b) $(\text{NH}_4)_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{S} = 2(\text{NH}_4)_2\text{S}_2\text{O}_7 + \text{S}$; (2) $4(\text{NH}_4)_2\text{S}_2\text{O}_7 + 6\text{SO}_2 = 2(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2(\text{NH}_4)_2\text{SO}_4$; (3a) $(\text{NH}_4)_2\text{S}_2\text{O}_8 = (\text{NH}_4)_2\text{SO}_4 + \text{SO}_2 + \text{S}$; (3b) $(\text{NH}_4)_2\text{S}_2\text{O}_8 = (\text{NH}_4)_2\text{SO}_4 + \text{SO}_2 + 2\text{S}$; (4) $4\text{S} + 4\text{O}_2 = 4\text{SO}_2$. Half of the trithionate and tetrathionate from reaction (2) is turned back into the cycle, the other half is decompd. by boiling into $(\text{NH}_4)_2\text{SO}_4$, SO_2 and S. The S is burned and the SO_2 goes back into the process. The net result is the oxidation of $(\text{NH}_4)_2\text{S}$ to $(\text{NH}_4)_2\text{SO}_4$ by O_2 from the air. Reactions (1a) and (1b) are easily seen to be a reduction of the polythionate to thiosulfate, the opposite of the well known oxidation of thiosulfate to tetrathionate by iodine. Reaction (2) at first defied explanation. In dil. solns. of thiosulfate SO_2 is absorbed only slowly and yields little polythionate but much sulfite and sulfate. Much thiosulfate is left unchanged. More concd. solns. absorb more rapidly and yield more polythionate. $\text{Na}_2\text{S}_2\text{O}_3$ in its own water of crystn. is quickly changed by SO_2 to equal parts of trithionate and tetrathionate. Further study showed this reaction takes place in 2 steps. First, as Salzer (*Ber.* 19, 1696 (1886)) showed, in the presence of K or Na arsenite the thiosulfate instead of being partly broken down with sepn. of S is mainly polymerized to pentathionate with no sepn. of S, the SO_2 remaining as sulfite. The second step is the reaction of the penta-

thionate with the sulfite yielding tetrathionate, trithionate and thiosulfate. Thus $5\text{Na}_2\text{S}_2\text{O}_3 + 3\text{SO}_2 = 2\text{Na}_2\text{S}_5\text{O}_8 + 3\text{Na}_2\text{S}_3\text{O}_6$ and $2\text{Na}_2\text{S}_2\text{O}_3 + 3\text{Na}_2\text{SO}_3 = \text{Na}_2\text{S}_5\text{O}_8 + \text{Na}_2\text{S}_4\text{O}_6 + 3\text{Na}_2\text{S}_2\text{O}_4$. The thiosulfate then reacts with more SO_2 . The net result is identical with Feld's reaction (2). The reaction between a sulfite and the pentathionate or tetrathionate was found to be so rapid and complete that it may be used for the volumetric determination of tetrathionate in a mixture with trithionate. A soln. of Na_2SO_3 whose iodine titer is known is mixed with the polythionate soln. and then titrated with I. The thiosulfate formed requires only half as much I as the sulfite. If pentathionate also is present the method shows the S in thionates higher than the trithionate, which does not react with sulfite. The presence of pentathionate is shown by a sepn. of S when NaOH is added, a reaction peculiar to pentathionate. If sulfurous acid is present it must be removed by an air current or addition of iodine before addition of sulfite. The use of catalyzer suggested by this study of the reactions removed the main difficulty in the Feld process, namely the slowness of the regeneration of the polythionates. There were other difficulties. Not all coke-oven gases contain 2NH_3 for each H_2S . Many have more NH_3 . Then SO_2 from sulfur or pyrite must be added, with care not to waste an excess. More troublesome are the gases which have more H_2S than 1 for 2NH_3 . Here the best remedy seems to be to add NH_3 . Success depends upon having in the gas 2NH_3 to each H_2S , but coke-oven gas varies during the coking period. Even a large number of ovens does not in practice give uniform gas. Const. chemical control is necessary.

J. J. MORGAN

The sulfur in heavy coal-tar oils. R. WEISSGERBER, Duisberg-Meiderich. *Brennstoff. Chem.* 2, 1-3(1921); cf. Weissgerber and Kruber, *C. A.* 15, 88.—The S compds. of tar oil are almost exclusively built up on the thiophene ring. *Thionaphthene* and *biphenylene sulfide* were isolated in pure form from crude naphthalene and crude phenanthrene, resp., and *methylthionaphthene* from crude methyl-naphthalene in two isomeric forms, m. 52° and 36° . Sepn. of the S compds. by means of metals (Na or Zn) is feasible, but too expensive for application to fuel oils. No process is yet known for sepn. of the S compds. from tar oil on a practical scale without destroying them.

W. B. V.

The continuous rectification of benzene. A. BARIL. *Chimie et industrie* 2, 1013-16(1919).—While before the war the use of benzene was increasing in France, its use was practically entirely as a carburant and for motor spirits. The latter required "benzol 90%," which is a mixt. of aromatics of d_{15} 0.880-0.883, and about 90% of which distills under 100° . The av. compn. is: Low boiling products 1%, benzene 85%, toluene 11%, solvent 3%. The last product is a mixt. of aromatics, there being 2 types in commerce, solvent naphtha 1 and solvent naphtha 2. The densities are 0.874-0.880 and 0.890-0.910, resp., while distn. should give not less than 90% between 120° and 160° for the first and 90% between 120° and 175° for the second. During the war, the development of the industry was rapid and complete. Modern plants for the continuous rectification of benzene were established. Complete sepn. by the discontinuous process required as high as 23 different fractionations. The app. for continuous rectification consists of 3 column stills each provided with heaters, dephlegmators and condensers. The crude benzene enters near the middle of the first column, the vapors formed passing to the dephlegmator and condenser while the unvaporized higher boiling liquids pass on to the next column, which they enter near the middle. Thus there is a continuous flow of crude benzene into the app., while from the condenser on the first column flow the head products, from that of the second, pure benzene, from that of the third, pure toluene, and from the base of the 1st column, the solvent naphtha. The advantages of the continuous process over the others, besides the purity of product obtained are its ease of control, simplicity of operation and app. and a steam requirement of but $\frac{2}{3}$ that of the other process. The paper is illustrated.

P. D. V. MANNING

The corrosion of metals by the phenols of low-temperature tar. UDO EHRHARDT AND GEORG PFLIEDERER. Mülheim. *Brennstoff Chem.* 2, 9(1921).—Various metals were shaken for 4 weeks with low-temp. tar fractions b. up to 270°, satd. with H_2O , in the presence of air. Al, 18% silicon-iron and "V₂A" steel (Krupp) did not lose in weight; Ni and rolled Fe were not badly attacked; Cu, Zn and Pb were the least resistant, but brass was less attacked than either Cu or Zn.

W. B. V.

Organization and equipment of by-product works. HAROLD J. HAILSTONE. *Gas J.* 153, 231-2(1921).

J. L. WILEY

Interrelations of fossil fuels (STEVENSON) 8.

Solid fuel. NOBILE C. TOMMASI AND HEINRICH DANNEEL. Can. 208,852, Feb. 22, 1921. A solid fuel consisting of a hard aggregate of metaldehyde crystals interpenetrating themselves mutually is prepd. by subjecting the crystals to pressure.

Distilling coal, wood or similar materials. W. THOMAS. U. S. 1,365,128, Jan. 11. In distn. of coal, wood or similar materials, a regenerating chamber is heated internally, purified gas is heated by passing it through the heated chamber and the heated gas is then passed into contact with the material to be distd. in a sep. chamber. Vapors produced, together with hot gases, are passed from the latter chamber and brought into contact with one surface of a double-surface condenser while at the same time cooled and purified gas is brought into contact with the other surface of the condenser. The purified gas thus partially preheated in the condenser is further preheated by passing it through the regenerating chamber and is then passed into the distn. chamber.

Removing water from peat. Can. 208,415, Feb. 8, 1921. A. TEN BOSCH. Peat resting on a grid in a vertical tower under gravity pressure is subjected to steam treatment under pressure.

Apparatus for heat-treating fuel briquets. J. F. LOVEJOY. U. S. 1,366,091, Jan. 18. The app. is especially adapted for heating and drying briquets with a binder of waste sulfite pitch.

Treating gas liquor to form fertilizers. GES. FÜR LANDWIRTSCHAFTLICHEN BEDARF, AND I. R. MANDELBAUM. Brit. 153,006, Oct. 25, 1920. Gas liquor is freed from NH_4 cyanide and thiocyanate and rendered suitable for use as a fertilizer by adding $(NH_4)_2S_2$ or S or by treating it with air or other agent to sep. S from the S compds., and distilling the liquor. The cyanide is transformed into thiocyanate, which remains in the retort.

Gas-washing and humidifying. J. P. RUTH, JR. U. S. 1,365,278, Jan. 11. Centrifugal force is employed for circulating liquid and gas such as coal gas, H_2O and a small amt. of oil in contact with each other.

Ammonium sulfate. J. BECKER. U. S. 1,366,111, Jan. 18. In the recovery of $(NH_4)_2SO_4$, moist tar-freed gas is passed through a portion of the satn. bath, to effect absorption of the NH_3 from the gas, and the NH_3 -freed gas is then superheated and passed through another portion of the satn. bath to effect evapn. and consequent pptn. of $(NH_4)_2SO_4$.

Ammonium sulfate. A. E. WHITE. Brit. 153,177, Nov. 14, 1919. In the "semi-direct" method of recovering NH_3 as sulfate from coke-oven gases the hot vapors from the NH_3 still are further heated by means of the waste gases from the coke ovens and then mixed with the cooled gases from the tar extractors, the mixt. then passing to the saturator; the heat thus supplied prevents diln. of the acid in the saturator by the H_2O present in the gases. A suitable app. is specified.

Process and apparatus for producing gas. FRANK E. MODLIN. *Can.* 208,885, Feb. 22, 1921.

Gas-producer and superheater. G. F. RENDALL. U. S. 1,366,213, Jan. 18.

Suction gas generators. STANLEY PHILLIPS. *Can.* 208,577, Feb. 15, 1921.

Tar extractors and scrubbers for gas. JNO. WELLS. *Can.* 208,198, Feb. 1, 1921.

Coke-quenching apparatus. G. A. and W. H. FLOOD. U. S. 1,365,974, Jan. 18.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Catalytic hydrogenation of *l*-rotatory Java oil fractions. WILHELM STEINKOPF AND FRITZ BEHRSDORF. *Dresden. J. prakt. Chem.* 101, 75-8(1920).—Hydrogenation of the *l*-rotatory fractions of Java petroleum by means of Pt black caused no change in the optical properties, thus showing that the *l*-rotation is not due to the presence of cholesterylene as previously reported (cf. *C. A.* 14, 3635). In 3 cases investigated, the fractions containing the greatest amt. of unsatd. compds. showed the least optical activity.

D. BREESE JONES

The relations between the asphalt and coke content of petroleum. WILHELM STEINKOPF AND HANS WINTERNITZ. *J. prakt. Chem.* 101, 82-92(1920).—Seventeen different oils were investigated. Their content of both hard and soft asphalt was detd., as well as that of the coke formed both *in vacuo* and at atm. pressure. Dctns. were made also of the % of coke resulting from both hard and soft asphalt. It was found that 40% of the hard asphalt present was converted into coke, and 40-60% of the soft asphalt. Distn. *in vacuo* yielded less coke than distn. at atm. pressure, especially in the case of oils rich in asphalt.

D. BREESE JONES

Scientific testing of hydrocarbon oils. JAMES A. BISHOP. *Shale Review* 2, No. 8, 15-6(1920).—Special reference is made to the testing of shale oils, and the requirements of a shale-oil chemist. A description of the five hydrocarbon branches is given, and recommendations are made for preventing the decompn. of the paraffin series. Lab. retort practice should be a duplication of large-scale work.

A. H. HELLER

Shale retorting and refining problems. M. BENNETT BLACKLER. *Shale Review* 2, No. 12, 3-4, 15(1921).—In certain cases too low a temp. of distn. gives undesirable products. On account of large losses of unsaturated compds. when acid is used for refining, it is suggested that work be carried on along the line of fractionally sepg. the diolefins from distillates by means of solvents, and in the case of lamp-oil distillates using the unsatd. products for the production of gasoline by a cracking process. S and diolefins can be practically eliminated by the use of fuller's earth at a high temp. and having the oils in a vapor state.

A. H. HELLER

Problems in the production of oil shale. L. C. KARRICK AND J. J. JAKOWSKY. *Salt Lake Mining Review* 22, No. 12, 25-7(1920).—Commercial considerations of refinability and usage of oil, makes it desirable to obtain as high a percentage of paraffins as possible. This is accomplished by heating slowly, low temp. and pressure, and avoiding recondensation of vapors. The theory of shale retorting is dealt with, and characteristics of American oil shales are given.

A. H. HELLER

Gasoline from natural gas. V. Hydrometer for small amounts of gasoline. R. P. ANDERSON AND C. E. HINCKLEY. *J. Ind. Eng. Chem.* 13, 144-5(1921); cf. *C. A.* 14, 3786.—The description of a hydrometer for the rapid detn. of the gravity of small amts. of gasoline, requiring only 4 cc. Temp. correction curves are included.

F. W. PADGETT

Comparative tests of lubricating oils (ANON.) 13. The commercial synthesis of

the higher fatty acids from hydrocarbons (FRÈRE) 27. The use of liquid fuels in industrial furnaces (CAUCHOIS) 21. Action of steam and gases on yields of ammonia from carbonization of oil shales and coal (FRANKS) 21. Resins from naphtha (U. S. pat. 1,365,423) 26.

Purifying hydrocarbon oils. D. T. DAY. U. S. 1,365,894, Jan. 18. Petroleum oils are freed from impurities such as acetylene hydrocarbons by treatment with Cu_2Cl_2 in ammoniacal soln.

Cracking hydrocarbons. W. F. RITTMAN and C. B. DUTTON. U. S. 1,365,605, Jan. 11. Hydrocarbon oils of relatively high b. p. are cracked in vapor phase under conditions of heat and pressure which will produce a large amt. of hydrocarbons b. below 30° . Naphtha of about 53° B \acute{e} . is condensed from the mixed vapors formed and the uncondensed vapors are passed through the naphtha to effect absorption of hydrocarbons of low b. p. from the vapors.

Vertical tube retort for cracking hydrocarbons in the vapor phase. W. F. RITTMAN. U. S. 1,365,602, Jan. 11.

Method of heating hydrocarbon oils during cracking in the vapor phase. W. F. RITTMAN and C. B. DUTTON. U. S. 1,365,603, Jan. 11.

Cracking hydrocarbon oils. W. F. RITTMAN and C. B. DUTTON. U. S. 1,365,604, Jan. 11. A hydrocarbon oil of relatively high b. p. is vaporized and the vapors are subjected to a cracking temp. and pressure. Products of high b. p. are condensed out of the resulting material and an intermediate fractional condensate is subjected to a re-cracking treatment.

Vertical retort for distilling oils from shale. J. H. GALLOUPE. U. S. 1,365,822, Jan. 18. The retort to which the shale is fed is of annular form in horizontal cross-section and is heated externally and internally.

"Reactive acid liquor" from olefinic gases, adapted for the production of alcohols. M. D. MANN, JR. and R. R. WILLIAMS. U. S. 1,365,043, Jan. 11. Olefinic hydrocarbon gases such as petroleum still gases are passed into intimate contact with H_2SO_4 in the presence of a non-reactive absorbent material such as petroleum oil in order to produce an "acid reactive liquor" which is adapted for use in the production of alcs. by heating with H_2O .

"Reactive acid liquor" from olefinic hydrocarbons. C. ELLIS. U. S. 1,365,044, Jan. 11. Olefinic hydrocarbon material such as volatile products from petroleum stills which also contains satd. liquid hydrocarbons is sulfated with H_2SO_4 and the acid ext. thus obtained is used for the further treatment of additional olefinic material to enrich it in compds. which are adapted for making alcs. or esters.

Treatment of gasoline or similar material with sulfuric acid. M. D. MANN, JR. U. S. 1,365,045, Jan. 11. A material such as gasoline containing unsatd. hydrocarbons is gradually treated with H_2SO_4 in the presence of a diluent for the acid such as H_2O while the temp. is maintained at about $15\text{--}20^\circ$ in order to obtain a product yielding alcs. on distn.

Ketones from cracked gasoline. C. ELLIS and A. A. WELLS. U. S. 1,365,053, Jan. 11. Cracked gasoline containing olefinic hydrocarbons is treated with H_2SO_4 of 1.8 sp. gr., the resulting acid sulfate ext. is sepd. and is then electrolytically oxidized to produce a mixed ketonic material adapted for use as a solvent of cellulose acetate.

Phenols from redwood. W. J. HUND. U. S. 1,365,407, Jan. 11. Communitated resinous redwood is heated in a retort to a temp. above 450° , and tar thus produced is fractionated to obtain an oily distillate b. $150\text{--}250^\circ$. This distillate is treated with caustic alkali soln., which dissolves a portion of it and mixed phenolic substances are

sepd. and recovered from the soln. They are stated to be marketable as a good grade of carbolic or cresylic acid.

Distilling wood. P. POORE. Brit. 152,741, July 15, 1919. Steam at a temp. of 180–270°, preferably 210–225°, is admitted to an externally heated retort used in the destructive distn. of wood, etc., in order to increase the yield of HOAc, naphtha, etc. Stationary cylindrical retorts, as described in 131,006 (C. A. 14, 115), or rotary retorts, as described in 141,417, may be used in carrying out the process.

23—CELLULOSE AND PAPER

A. D. LITTLE

Acetolytic decomposition products of cellulose. R. PROSIEGEL. *Zellstoffchem. Abhandlungen* 1, 8–24, 25–41 (1920).—Cellulose (cotton) was acetylated by treating 60 g. cotton, 300 g. Ac_2O , 350 g. AcOH and 65 g. H_2SO_4 , at a temp. not over 30° for various periods of time. The products were then fractionated with different solvents, the results being followed by detg. the AcOH content, the rotation, and m. p. From these values it was concluded that the ether-sol. acetates were probably octaacetates of a biose, the benzene-sol. acetates were dextrin acetates most distant from true cellulose triacetate, while the benzene-insol. acetates were closely related to the true cellulose acetate. From the Et_2O -sol. acetates the carbohydrate was obtained by sapon. with cold 0.5 N $\text{Ba}(\text{OH})_2$. The benzene-sol. acetates were decompd. by sapon. with 2 N alc. KOH . The carbohydrates were fractionated by means of alc.- H_2O mixts. In this way the sapon. product from the Et_2O -sol. acetates yielded a new biose, *celloisobiose*, $[\alpha]_D^{25}$ 23°, sinters 165°, m. 190°; 200 mg. gives 220.2 mg. Cu when heated with Fehling soln., that is the reduction capacity is 56.4% of that of dextrose. It is not fermented by yeast, but upon inversion with HCl gives 2 mols. dextrose. *Osazone*, m. 155–160°, $[\alpha]_D$ Auer = –46.1°. The purest dextrin which was isolated has $[\alpha]_D$ 13.6°, a copper no. of 74.3, and a reduction capacity of 38% that of glucose. There appears to be no relation between the decompn. of starch and of cellulose through the acetates, even though both yield the same end product, glucose. C. J. WEST

Titration of the sulfite waste liquor. RUDOLF SIEBER. *Zellstoffchem. Abhandlungen* 1, 95–104 (1920).—The old and the more recent methods are compared. Of these the new Sander method and the modified Höhn (old) method are suitable for the works lab., or the works itself. C. J. WEST

Investigation of the compounds from the alkaline cooking of wood. IV. Colloidal lignin solutions from alkali liquors. ERIK WAHLBERG. *Zellstoffchem. Abhandlungen* 1, 92–95 (1920).—The attempt is made to fractionate the alk. liquor by dialysis. A study is made of the compds. isolated by dividing the cooking period into 3 sections, but as might be expected, little progress is made. Cf. C. A. 14, 170. C. J. WEST

Simplification of the methods for the investigation of plant materials. II. WISLICENUS. *Zellstoffchem. Abhandlung* 1, 77–92 (1920).—Suggestions are made as to methods of prepg. the material for analysis, methods of ashing, and methods of detg. the moisture and dry matter. C. J. WEST

Determining the lime content of fresh sulfite liquors by Feld-Sander's method. RUDOLF SIEBER. *Zellstoffchem. Abhandlungen* 1, 1–8 (1920).—See C. A. 15, 39. C. J. WEST

Chemical composition of wood pulp. CARL G. SCHWALBE AND ERNST BECKER. *Zellstoffchem. Abhandlungen* 1, 42–52 (1920).—The authors have collected the analytical figures for 57 samples of wood pulp, and have discussed the meaning of each detn. and also the characteristics of the various types of wood pulp. C. J. WEST

Utilization of the reed (*Phragmites communis* Trin) for the manufacture of pulp. HERIG. *Cellulosechemie* 1, 65-76, 77-83, 85-93(1920).—This is the report of a complete lab. and exptl. plant study of the use of the reed as a raw material for paper pulp. The soda process is used for cooking the reed; the pulp may be bleached white, though the process as yet is too complicated for practical purposes. The resulting paper is very porous, and has about the same strength properties as ordinary writing paper. The work is important as showing how such a study should be carried out.

C. J. WAST

The hydrides of naphthalene, anthracene, phenanthrene, phenol and their derivatives (FRYDLENDER) 13. Lignin and lignin reactions (KLASON) 10. Constitution of the lignin of pine wood (KLASON) 10. Ketones from cracked gasoline (as cellulose acetate solvent) (U. S. pat. 1,365,053) 22.

Ornamental paper. C. L. THUNERT and K. HEINIG. Brit. 153,276, May 19, 1920. An ornamental paper or fabric suitable for bookbinding, wall covering, note-case covers, and as an imitation of parchment, pigskin, wood and cloth graining, and other materials, is produced by applying a layer of tissue or like paper or fabric to a paper backing, the layer being colored by a wet process, the colors being rubbed on to produce different shades. A transparent layer is applied on the colored layer and brushed and coated with a varnish-like mass. Irregular raised veining and graining is produced by applying the tissue or like in a more or less crinkled state.

Sizing. F. J. MORRISON. U. S. 1,365,715, Jan. 18. A compn. adapted for sizing paper or pulpboard is formed of H₂O mixed with Na silicate 3-15, glue or a similar org. adhesi. 1-7 and a filler such as pottery clay 1-8 parts.

Non-absorbent pulp-board. F. J. MORRISON. U. S. 1,365,716, Jan. 18. Pulp-board or wood or paper is rendered non-absorbent and suitable for receiving paint by coating and partially impregnating it with a sizing compn. such as that described in U. S. pat. 1,365,715 (above).

Dyeing cellulose acetate. E. PRINCE. U. S. 1,366,023, Jan. 18. Cellulose acetate is prepd. for dyeing with usual dye solns. by treatment with a dil. NaOH soln. containing NaCl or other sol. salt which promotes uniform action.

Semicellulose. T. and E. KITTELSEN. U. S. 1,365,039, Jan. 11. Pieces of wood which are cut or bored lengthwise are treated with cleared black lye with the use of steam and then treated with fresh NaOH soln. from electrolyzers mixed with cleared black lye while being boiled with steam and afterward washed and ground or crushed to obtain a semicellulose paper pulp.

Nitrocellulose composition. L. E. BARTON and H. A. GARDNER. U. S. 1,365,882, Jan. 18. A white opaque compn. adapted for the manuf. of molded articles or sheets is formed of nitrocellulose, a Ti oxide pigment and camphor.

24—EXPLOSIVES AND EXPLOSIONS

C. E. MUNROE

Some electrical causes of dust explosions. DAVID J. PRICE. *Elec. Rev.* 78, 179-81(1921).—It is shown that the theory that an elec. spark will not ignite inflammable dust is not correct and that explosions have occurred in factories because of elec. sparks, the breaking of elec. light bulbs in dust filled atms., and static electricity.

D. I. GLERIM

Waste disposal from war manufactures (STOOFF) 14. Binary equilibria of some nitro derivatives with toluene (GIWA) 10.

Explosive. J. H. BABCOCK. U. S. 1,366,048, Jan. 18. An explosive adapted for military purposes is formed of dinitro-*p*- and dinitro-*o*-dichlorobenzene. The explosive m. 65–85° and at lower temps. is a solid cryst. substance, capable of withstanding the KI test. Picric acid may be used in solid soln. in the mixt.

Explosives. C. F. BEAKBANE and J. ARNOT. Brit. 153,123, Aug. 14, 1919. The pat. describes method and app. for the recovery of NH_4NO_3 from explosives such as amatol and ammonal employed in shells, in which the explosive is removed from the shells by the circulation therethrough of hot H_2O under pressure, the resulting soln., after pptn. and sepn. of the contained trinitrotoluene, being evapd. down to cause crystn. of the NH_4NO_3 . According to the invention, H_2O at 86° and under a pressure of 25–55 lbs. per sq. in. is circulated until the liquid attains a d. of 50° Tw., and, after sepn. of the trinitrotoluene, is coned. to 72° Tw. for crystg. out the NH_4NO_3 . A suitable app. is specified.

Ammunition. E. W. BRANDT. Brit. 152,972, Apr. 22, 1919. The envelopes of ordnance and other cartridges and propellent charges are made of celluloid or like highly inflammable material, instead of silk, amiantine cloth, thick paper, cotton, or thin metal.

Hydrocarbon gas cartridge. K. F. L. WOLF. Can. 207,947, Jan. 25, 1921. A gas-producing cartridge comprizes alternate layers of a carbide and a hydrocarbon oil held by a suitable absorbent such as sawdust.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Colloidal chemical investigation as a foundation for the theory of the process of dyeing cellulose. R. HALLER and A. NOWAK. *Kolloidchem. Beihefte* 13, 61–136 (1920); cf. *C. A.* 6, 1529; 8, 1015, 1673, 2485; 11, 3441; 13, 1021.—Six classes of dyes, the substantive for cellulose, the basic, the vat and S dyes, the mordant dyes, the diazo dyes and aniline black were examd. ultramicroscopically and microscopically in soln., on the fiber, and after the fiber had been dissolved away by copper ammonium hydroxide, and by dialysis of the dye solns. In every case the conclusion is reached that the active dye is colloidal and has suffered no chem. change in the process of dyeing the fiber. There are two kinds of dyeing; a deposition of the dye on the surface of the fiber, *apposition*; a more or less complete permeation of the membrane walls, *intussusception*. Dyeing of cellulose depends on an apposition of the dyestuff; intussusception alone never occurs, but frequently accompanies apposition and indicates a high degree of dispersion of the dyestuff. Fastness, tone and depth and uniformity of color depend on a high degree of dispersion of the dye. Since dye solns. tend to become less dispersed on standing it is customary to add the dye to the vat only as fast as the fiber will take it up. In practice there are many instances of change in color as a result of change in dispersion, as in the steaming of Turkey red and the change of indigo gray to indigo blue. That dyeing is not a chem. reaction with the fiber follows from the physical properties of the dye after the fiber has been dissolved away, from the fact that $\text{Al}(\text{OH})_3$ and BaSO_4 can be dyed, and from the fact that insol. suspensions will dye materials and that an insoluble dye powder may dye material by being pressed into it.

H. I. MATILL

The use of the tint photometer in the evaluation of dyestuffs and pigments. H. B. GORDON. *Color Trade J.* 7, 175–80(1921).—The tint photometer may be used for

the detn. of the relative color values of 2 dyestuffs, and "presumably of pigments," whether sol. or insol. by the use of reflected instead of transmitted light. The results should be checked by trial dyeings. The method demands a numerical expression of color values, which may be obtained with instruments like the Lovibond tintometer Hess-Ives tint photometer, and others. The probable application of Beer's law of light absorption to light reflected from an opaque, colored sample is shown by an algebraic and a graphical study of the data obtained, with a Hess-Ives tint photometer, from the color values of samples of cloth and yarn dyed with varying % of dyestuff. The mathematical relationship between color value, x , and % dyestuff, y , then expressible is $x = K.y^a$, where K and a are consts. derivable for each case from the data. This formula is most conveniently used in the logarithmic form, $\log x = \log K + a \log y$, graphically shown on logarithmic paper. Two possible applications of the law are illustrated. One consists in making a log plot of the data obtained from the standard sample of dye, making a trial dyeing with the sample to be tested and comparing the color value of this dyed sample with the plot of the standard to find the corresponding %. A single redetn. of the color value of the standard sample for one % at the time of making the test on the dyed sample eliminates any error due to slight changes in the adjustment of the instrument from time to time. Thus if the standard had a green value of 50 at 0.31% and the sample one of 50 at 0.49%, the two relative concns. are as 49 to 31 or the sample is 63% the strength of the standard. The second application consists in studying the solid dye-stuffs, suitably diluted with inert material as dextrin, and the color values compared to these of the standard. Some dyes change hue on such dilution, which makes the checking of results with the dild. mixts. unreliable. The method for studying pigments is similar, using ZnO and linseed oil for the dild.; the study of pigments has been exptl. only. A. K. JOHNSON

The A. B. C. of direct cotton dyestuffs. OSCAR R. FLYNN. *Textile World J.* 58, 1982-7(1920).—A discussion of the development of the American industry in these products. CHAS. E. MULLIN

Iron buff printing pastes. RAFFAEL SANSONE. *Textile World J.* 58, 2071(1920).—To prep. fairly pure $\text{Fe}(\text{OAc})_2$ soln. producing neat bright brown prints of superior color mix warm solns. of 500 parts $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 500 parts H_2O , and 440 parts $\text{Pb}(\text{OAc})_2$ in 500 H_2O . Let the ppt. of PbSO_4 settle out, dil. the soln. to 1.15 sp. gr. and store in closed containers. A less pure soln. can be made by dissolving iron turnings in the calcd. quantity of crude AcOH (d. 1.1-1.5) and dilg. to d. 1.15. Another method of prepn. is to dissolve 500 parts $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 500 parts boiling H_2O . Treat this with 200 parts 98% Na_2CO_3 in 500 parts H_2O and let the FeCO_3 settle. Wash the ppt. several times by decantation, filter and dry. Dissolve the dried ppt. in as little as possible crude AcOH (1000 parts AcOH (d. 1.045) dissolve about 250 parts ppt.). The ferrous acetate solns. are dild. to 1.15 sp. gr. and thickened with an equal wt. dextrin or gum thickening paste, with as little heating as possible, and the resulting color paste is printed directly afterwards. As a rule after printing, drying and ageing, the goods are passed through a 1% chalk bath at 70-5°. The substitution of wheat or corn starch or bran as a thickener to replace the dextrin or gum is suggested. A very cheap paste without AcOH is made by mixing 20 parts FeSO_4 (d. 1.15) or $\text{Fe}(\text{NO}_3)_3$ soln. with 60 parts glycerol, and slowly adding to the resulting mixt. 20 parts NH_4OH (d. 0.9) with agitation. When an equal wt. of suitable thickener is added it is ready to print. The colors are fixed by drying, steaming or hanging. The chalk treatment increases fastness and brightness. A small addition of tannic acid to the paste gives a grayish brown; yellow prussiate makes it bluer; Cr gives near a khaki shade, and Mn darker shades. CHAS. E. MULLIN

Analysis of mixed wool and cotton fabrics. DUYK. *Ann. chim. anal. chim. app.* 2, 324-30(1920).—D. recommends the following: Cut up 10-15 g. of the material and

dry at 100° to 105°; treat with appropriate reagents to remove size, filling material, etc., wash, dry, and weigh. Then heat with 2% NaOH soln. in a covered vessel on the water bath to a max. temp. of 90° and continue the heating at this temp. for 20 min.; remove the cotton residue, wash it with H₂O, then acidified H₂O, and finally with H₂O, and dry at 100° to const. wt. Then calc. the amts. of cotton and wool on the basis of the official limits for moisture, viz., 17% for carded wool, 18.5% for combed wool, 8.5% for cotton, and 10% for silk. For the sepu. of silk from wool, boil the sample 2 min. with ZnCl₂ soln. (d. 1.65).

F. W. SMITHER

Testing the strength of fabrics. A. J. TURNER. *Textile World J.* 58, 1550-63 (1920).—This is an abstract of a paper presented before the Textile Institute upon breaking, bursting, tearing and impact testers, resistance to wear and weather, effect of conditions on tests, relation of fabric strength to yarn strength, effect of weave, etc.

CHAS. E. MULLIN

Drying woollen and worsted fabrics. EVERETT H. HINCKLEY. *Textile World J.* 58, 2991-3 (1920).—Discussion of uneven or cloudy piece dyeing due to "improper distribution or circulation of heat in dryers."

CHAS. E. MULLIN

Use of hydrogenated oil in the textile industry. ELTON R. DARLING. *Oil, Paint and Drug Rep.* 99, No. 3, 50D (1921).—A brief review of the manu. of hydrogenated oils. These have successfully replaced tallow and other compds. used as softening agents in the textile industry.

F. A. WERTZ

The partial disinfection of mulberry leaves in the feeding of silk-worms. ROSA SACCHI. *Staz. sper. agrar. ital.* 52, 332-48 (1919).—The results of previous expts. (*Staz. sper. agrar. ital.* 50, 49-68 (1917)) lead to these conclusions: (1) There is a sensibly less consumption of leaves washed in H₂O or in aqueous solns. of "Lysiformio" or "Tachiolo" than of non-treated leaves. (2) Larvae fed with moist leaves weigh more than those whose food is dried leaves, though consuming less. (3) Treatment with disinfectants does not hinder the manifestation of cases, though sporadic, of flaccidity and of meagerness. (4) The silky covering of cocoons obtained from larvae fed with partially disinfected leaves weighs more than that from larvae fed with untreated leaves. This greater wt. is also met with in cocoons of larvae fed with leaves washed with cool or boiling H₂O. (5) Feeding with washed leaves favorably influences the quality of the silk, particularly as to length, tenacity and elasticity as well as to wt. of floss silk that can be made into skeins. The results of 3 consecutive years' expts. here reported yield the following conclusions: (1) "Tachiolo" and "Lysiformio" are not efficacious means of combating flaccidity. (2) The use of these disinfectants in aq. solns. does not favor the "vegetative development" of the silk worm nor does it increase their yield in cocoons but often diminishes it through an increase in the mortality of the worms. (3) Disinfection increases the wt. of the crysalis because of a greater quantity of H₂O and diminishes the percentage of silky covering in the cocoons. (4) The quality of the silk is not modified by disinfecting solns. For these reasons it is not advisable to use "Tachiolo" or "Lysiformio" in the quantities or manner tried up to now; other substances or different means of application may solve the serious problem of the battle against flaccidity.

ALBERT R. MERZ

Some applications of the sulfonated products of seed and fish oils (SCURTI, FUBINI) 27. Carbazole-blue and carbazole-violet (COPISAROW) 10. Cyanine dyes. Constitution of pinacyanol (MILLS, HAMER) 10.

Disazo dye. T. H. LEAMING. U. S. 1,365,040, Jan. 11. A disazo dye is made by the combination of *p*-nitroaniline, *o*-anisidine and 2-amino-8-naphthol-6-sulfonic

acid, which is a brownish black powder sol. in H_2O with a reddish blue color, sol. in alc. and in H_2SO_4 . It dyes animal and vegetable fibers blue-black shades which can be developed on the fiber.

Trisazo dyes. H. LEVINSTEIN and J. BADDILEY. U. S. 1,365,706, Jan. 18. Dyes adapted for fixation on vegetable fiber by after-treatment with CH_3O are prepd. by coupling 2 mols. of resorcinol with tetrazo compds. of the type $-N:N-D_2-N:N-(2).OH(1).HO_3S(3).NH.CO.C_6H_4-N(6)$ in which D_2 is the nucleus of a diamine containing at least 2 aryl nuclei such as $-C_6H_4-N-O-N-C_6H_4-$ or a thioaryl nucleus. These dyes are orange, red or brown.

Anthraquinone derivatives and dyes. R. B. RANSFORD. Brit. 153,055, June 21, 1918. Condensation products, probably azomethine compds., are obtained by heating 1-amino-2-methylanthraquinone or its substitution products, or isomeric amino-2-methylanthraquinones, or 2-methylanthraquinone itself, with aromatic nitro compds. in the presence of alk. reagents; primary aromatic amines may be added to the reaction mixt. The products are vat dyestuffs, and may be hydrolyzed by acids to give 1-aminoanthraquinone-2-aldehyde, or its substitution products or isomers, or anthraquinone-2-aldehyde, resp. Numerous examples are given.

Dyeing apparatus. E. W. MORGAN. U. S. 1,365,936, Jan. 18.

Artificial silk threads from viscose. J. CLAYTON. U. S. 1,366,162-3, Jan. 18. Mechanical features relating to the pptn. and twisting of the fibers.

Nozzle for introducing viscose filaments into a precipitating bath. J. E. CRIGGALL. U. S. 1,366,166, Jan. 18.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Decoloration of Prussian blue by oxidized oils. F. FELIX. Berlin-Wilmersdorf. *Chem. Umschau*. 27, 242-3(1920).—The cross-section of a green or blue piece of linoleum frequently shows a white center. This color change is due to the reduction in the pigment of Prussian blue to Prussian white, $Fe_3Fe(CN)_8$, by the oxidized oils in the presence of moisture; it reverts to Prussian blue on exposure to air and light. Similar observations have been made by Landgrebe ("Über das Licht," 1834, p. 101-3) and Desmottier ("Res. sur la décoloration spontanée du bleu de Prusse," Paris, 1801, p. 32 and Gilberts, *Ann.* 10, 363).

P. ESCHER

Solvent losses in relation to costs and yields. CLARK H. BENNETT. *Paint, Oil and Chem. Rev.* 70, No. 18, 12(1920).—The use of solvent recovery systems (type unstated) is urged for paint and varnish thinning at elevated temps. Material cost figures of varnishes, etc., should be based on unit quantities delivered to shipping containers and not on invoice prices. The actual cost price must include in addition factory, container and overhead costs.

R. L. BROWN

The hydrides of naphthalene, anthracene, phenanthrene, phenol and their derivatives (FRYDLENDER) 13. The use of the tint photometer in the evaluation of pigments (GORDON) 25. Preparing glass, china, etc., for varnishing (Ger. pat. 319,744) 19. Acetic ester mixture (for varnish solvent) (U. S. pat. 1,365,049) 10.

Paints. A. HUTCHISON. Brit. 153,081, July 28, 1919. A non-inflammable and waterproof paint consists of ZnO , boiled oil, "petrified liquid" (consisting of H_2O and concd. size), Na silicate and $NaCl$.

Paint for masonry. S. W. CAMP. U. S. 1,365,372, Jan. 11. A paint adapted for use on masonry is formed of white lead 5, silica 3, varnish 1, linseed oil 1, drier 1 and turpentine 1 part.

Heat-radiating enamel. M. F. GANNON. Brit. 152,921, Mar. 4, 1920. A cylinder or other engine or machine part is coated with a protective and heat-radiating enamel containing copal, linseed oil, and lampblack. After coating, the article is stoved at a temp. of about 260° for about 4 hours. Preferably the article is coated twice, and is stoved after each coating.

Ultramarine. J. B. GRUMET and A. GUILLOCHIN. Brit. 152,916, Feb. 14, 1920. Sulfites or bisulfites of the alkalis, or mixts. of these salts are used in the manuf. of blue and green ultramarines to replace wholly or partially the alkali carbonates or sulfates usually employed. The Na_2SO_3 obtained as a by-product in the prepn. of phenol is particularly suitable for this purpose. In an example, the furnace charge consists of kaolin, Na_2SO_3 , S, and a reducing agent such as resin.

Coating-compositions. FREESES PATENT EISENSCHUTZ UND SCHRAUBENWELLENBEKLEIDUNG FÜR SCHIFFE GRS. Brit. 153,293, Oct. 4, 1920. A preservative coating compn. consists of 3-5 parts of red lead, 1-2 parts of wood-tar, and a diluent such as turpentine or xyloidin. Pasteboard coated with this material may be used in elec. insulation.

Varnish adapted for use on aircraft. S. E. GROVES. U. S. 1,366,256, Jan. 18. A cellulose ester varnish (which may contain celluloid, acetone, alc. and C_6H_6) is mixed with waxes such as beeswax and paraffin to retard evapn. of the varnish while it is being applied.

Resins from naphtha. S. P. MILLER and F. H. RHODES. U. S. 1,365,423, Jan. 11. In producing resins from naphtha, the latter is washed with an acid soln. such as 3% aq. HCl soln. after polymerization of polymerizable substances in the naphtha, in order to effect neutralization and ready sepn. of the washing liquid.

Removing ink from writing paper and preparing it for re-use. H. GETHG. Ger. 321,545, July 26, 1919. The paper is passed in succession through four baths; (1) a soln. of 2.5 kg. $(\text{HOCO})_2$ and 2.5 kg. glycerol in 25 kg. H_2O ; (2) 250 g. KMnO_4 in 25 kg. H_2O ; (3) 2.7 kg. $\text{Pb}(\text{OAc})_2$ in 25 kg. H_2O ; (4) 2.5 kg. $\text{Al}_2(\text{SO}_4)_3$ in 25 kg. H_2O . The first bath softens the writing, the second removes all residues of the ink, the third and fourth prepare the paper, after drying and calendering, for re-use.

Printing process. H. FERREGAUX. U. S. 1,365,058, Jan. 11. A glass plate is moistened with H_2O , a design is drawn upon it with an Al stylus, the plate is dried, inked with a printing ink containing glycerol and is then employed for printing impressions of the inked design.

27—FATS, FATTY OILS AND SOAPS

A. H. SCHERUBEL

Annual review of fats, oils and waxes for 1919. W. HERRBIG. *Z. deutsch. Öl-Fett-Ind.* 40, 486-8, 519-20, 533-4, 568-9, 597-9, 616-9, 634-6, 664-6, 697-9, 712-3, 725-7, 742-4, 760-2, 775-9, 793-6, 809-12(1920); cf. C. A. 14, 2096.—A thorough and detailed review is given under the following captions: (A) Physical properties; (B) chem. behavior and const.; (C) analysis; (D) investigations of vegetable oils and fats; (E) animal fats and waxes; (F) special analytical and scientific investigations; (G) technical prepn. and application, refining, cleavage, glycerol substitutes, soap manuf., special products, margarine.

P. ESCHER

The commercial synthesis of the higher fatty acids from hydrocarbons. J. FRÈRE. *Rev. prod. chim.* 23, 621-7(1920).—A review of recent work, carried out mostly in Germany, on the oxidation of commercial hydrocarbons, and especially paraffin, to higher fatty acids for use in the soap industry, and to fatty anhydrides and esters which have a nutritive value; including the work of Harries and co-workers, Schaal (Ger. patent 32,705, filed Sept. 27, 1884, lapsed Feb. 7, 1894), Schmidt (C. A. 12, 94), Bergmann, Kelbar, Ad. Grün, Franz Fischer and Wilhelm Schneider, H. H. Frank, K. Loeffl, Thomas T. Gray (C. A. 9, 3358), and D. Holde. A. P.-C.

The hydrogenation of fats. *L'âge de fer* 36, 769-71(1920).—Brief review of the chemistry and history of hydrogenation and of some of the patents in connection with the process. A. P.-C.

Microchemical tests for oils and fats. L. ROSENTHALER. Bern. *Schweiz. Apoth.-Ztg.* 58, 545-9, 562-7, 578-83(1920).—To 2 mg. of the oil on a slide add a drop of the satd. alc. KOH or NaOH reagents. Crystn. takes place at once with arachis and olive oils; rape, castor and poppy oils yield characteristic forms. Cod-liver oil is unique in giving no crystals with KOH; it yields crystals with NaOH. The effects of KOH and NaOH are generally different. With KOH, the seeds of peanuts, almonds, peach, cacao and ricinus show the same effect as their resp. oils; this is true of ricinus seeds with NaOH also. Sketches of the crystals are shown. S. WALDBOTT

The determination of the iodine number in oils and fats. W. OLSZEWSKI. *Pharm. Zentralhalle* 61, 641-2(1920).—A review of methods with bibliography. H. A. S.

The castor oil industry. J. H. SHRADER. Bur. Plant Ind., U. S. Dept. Agr., *Bull.* 867, 1-40(1920).—In reviewing this industry an account is given of the process of manuf., properties, compn. and uses of the oil, and methods of refining. Evidence has been obtained that a good grade of No. 1 oil can be obtained by extn. with volatile solvent. Highly acid dark oil can be refined by alkali but not highly bleached, while low acid oils can be refined and bleached almost to water whiteness. Cf. C. A. 14, 2097. W. H. ROSS

Salvaged rape seed. C. GRIMME. *Seifensieder-Ztg.* 48, 4(1921).—A cargo of seed sunk during the summer of 1920 was examd. after being in the H₂O 8-12 days. The oil content decreased, the color of the oil increased and its sp. gr. and sapon. no. rose, while the I no. and n_D fell. The nutritive material decreased. E. S.

Fish oils with high content of unsaponifiable matter. O. STREINER. Osnabrück. *Z. deutsch. Öl-Fett-Ind.* 40, 809(1920).—The analytical results of 5 samples of various fish oils show an unsapon. matter of 11.90—35.0%. This unsapon. matter is free from glycerol and is sol. in alc. and boiling AcOH, in some cases forming on cooling a cryst. magma. The oil with 35% unsapon. matter is pronounced a genuine sperm oil and the unsapon. consists probably of higher alcs. Further work is being done. P. ESCHER

Some applications of the sulfonated products of seed and fish oils. F. SCURTI and A. FUBINI. *Stas. sper. agrar. ital.* 52, 436-46(1920).—NH₄ salts of the sulfoleates and the sulforicinate were prepd. for the purpose of comparing their behavior. The NH₄ sulforicinate was prepd. by slowly pouring 66° Bé. H₂SO₄ on castor-oil, continuously agitating and keeping the temp. below 35°. After 24 hrs. standing 2-3 vols. H₂O were added, the oily stratum was sepd. from the acid glycerol stratum and washed with Na₂SO₄ soln. until the wash-water was only feebly acid and then NH₄OH was added till a small portion dild. with H₂O gave a perfectly clear soln. The NH₄ sulfoleate was prepd. by dropping 66° Bé. H₂SO₄ on com. olein in equimol. quantity, stirring continuously and keeping the temp. below 35°. NH₄OH was then added to the sulfonic acid sepd. from the acid liquid until the reaction was neutral. Whale, cod-fish and

tunny oils were treated similarly to the olein, the temp. not being permitted to rise above 40–45°. The products thus prepd. showed the following consts.:

	Tunny.	Whale.	Cod-fish.
% H ₂ O.....	30.89	24.46	15.50
Acidity index (mg. KOH per g. substance).....	125.1	101.6	154.5
I index.....	15.8	12.6	25.5

They were sol. in H₂O but left to themselves became insol. through polymerization and formation of internal anhydrides. Transformed into the resp. NH₄ salts they gave slightly turbid liquids of reddish yellow or brownish red color. Expts. show that the sulfoleates, whether prepd. from seed oils or fish oils, present a strict analogy to the sulforicinate, which they can replace, if not entirely, in the greater part of their varied applications. They serve very well for bringing about the wetting of raw cotton, for the dyeing of cotton with "malsequenti" dyes such as the yellow "Bisamine G," for the dyeing of vegetable fibers with vat dyes such as "Ciba blue B.B." and "Algol red R.," for the soln. and emulsification of mineral oils for use as lubricants, and for the softening of hides in tannin and chrome tanning. Unlike the sulforicinate they do not lend themselves to dyeing vegetable fibers with alizarin. Solns. of the sulforicinate remain clear and unaltered on standing, while the sulfoleates, generally rendered turbid by foreign matter contained in the com. fats, sep. on long standing into 2 layers, one reddish yellow, mobile and perfectly clear, the other whitish and of buttery consistency which floats on the first.

ALBERT R. MERZ

Rubber-seed oil. ANON. *Chem. News* 121, 206(1920).—Expts. on extg. oil from the seeds of the Para rubber tree have given encouraging results. It was believed that the oil would prove a substitute for linseed oil, but as yet this belief is not warranted. It has been ascertained that seed on storage deteriorates and produces an oil contg. up to 25% free fatty acids, and that such an oil is not suitable as a substitute for linseed oil. Considerable progress has been made in the work of refining the oil. Expts. on the prepn. of a boiled oil have shown that a satisfactory product can be obtained from a raw oil free from fatty acids.

E. SCHERUBEL

The production and utilization of corn oil in the United States. A. F. SIEVERS. *Rur. Plant Ind., U. S. Dept. Agr., Bull.* 904, 1–23(1920); *Cotton Oil Press* 4, No. 9, 50–60(1921).—An account is given of the prepn. of corn oil from the germ of corn kernels, a by-product obtained in the manuf. of certain staple corn products, together with a discussion of the economics and future of corn-oil production. W. H. ROSS

Extraction of oil cakes. P. POLLATASCHKE. Heidelberg. *Z. deutsch. Öl-Fett-Ind.* 41, 1–4(1921).—Illust. Since 1916 Germany has been compelled to ext. her *rape-, linseed- and buckwheat-oil-cakes*, mainly by means of benzene and high boiling benzine, in order to increase the oil supply, but the extd. oil is difficult to purify and is fit for technical use only, while the oil-free residual meal from rape- and linseed-oil is not relished by live-stock. Extn.: The ground cake is placed in silo-hoppers and fed into vertical tanks, fitted with agitator and steam coil and containing near the bottom a cloth filter stretched between two screens. The solvent, which may be a weak ext. of the previous charge, is pumped into the extractor-tank and kept at 30 to 40°. When drawn off, the first portions are fully satd. with oil and can be run directly into the vacuum still while the later, dil. portions are run through a 2nd and 3rd extractor. The end of extn. is detd. by evapg. from paper a small sample; it should leave no oil spot behind. The exhausted meal is freed from its solvent by direct steam at 104 to 105°, while the oil is freed from it in the vacuum still. On account of steam condensation the exhausted meal absorbs 22 to 26% H₂O and must be dried to 10% or 8% before it can be sacked. The present poor quality of solvents causes the recovered

oil to contain so much coloring and mucilaginous matter that it cannot be used for edible purposes.

P. ESCHER

Oil extraction by electrolysis. ANON. *Chem. Age* (N. Y.) 28, 407-10(1920).—The mechanical equipment consists of a series of iron pipes 2 in. in diam., through each of which passes axially a C rod 1 in. in diam., thus leaving an annular space of $\frac{1}{2}$ in. The C rod rests in insulators outside so that it becomes the negative electrode, and the Fe pipe the positive electrode. To one end of each pipe is screwed a right-angle end fitting, which is connected to a similar fitting on the next pipe by insulating hose. From 12 to 20 of these pipes are connected in series, so that any particle of material is subjected to as many independent applications of current as there are oils. The raw material to be treated is ground according to the nature of the substance so as to permit easy mixing with the electrolyte and to facilitate pumping to a feed tank, from which it is pumped by a gear pump into the base of the electrolytic unit and through the annular space between the C and the pipe. The material emerges in the form of an emulsion. The remainder of the process is mechanical and consists of sepn. of solids and their washing and the sepn. of the oil from the electrolyte in the emulsion. The theory of the process is that the current in its passage through the mass bursts the fat cells instantaneously. The equil. which has existed between the fat cells and the electrolyte is destroyed by the current action with a consequent setting up of osmotic pressure within the cells sufficient to rupture or otherwise cause the discharge of their contents. Practically the entire fatty content of the material is released. Tests in cod livers show a recovery of 99.75% of the fat content. The com. application of the process is almost unlimited; animal fats can be rendered instantaneously. Vegetable oil-bearing material requires a different electrolyte and gives better yields when subjected to somewhat higher temps. A comparison of this process with the oil process on marine oils shows the following advantages: (1) Practically 100% of the oil content of livers is extd.; (2) the process is odorless; (3) the oil is all of one grade (the best); (4) the process is continuous and automatic; in 3 min. the finished oil is running into the tierces; (5) the residu is automatically thrown out and may be dried for fertilizer; (6) the cost to produce 400 lbs. of oil is about 6 cents; (7) the floor space is very small and the capacity only limited by the speed of the pump and the annular space between the electrodes. A complete unit for the production of 400 bbls. of oil per day of 10 hrs. operating on fish livers would require the following equipment: 1 feed tank, 1 pump, 1 3-h. p. motor to operate the pump, 1 electrolytic unit. One $3\frac{1}{2}$ -k.w. generator to supply current, 1 rotating screen, 1 weir tank, 1 centrifugal separator and 2-h. p. motor to drive same, 1 centrifugal clarifier and a 1-h. p. motor to drive same. The floor space required is $5 \times 5 \times 5$ for the electrolytic unit, $6 \times 4 \times 4$ for the weir tank and $2 \times 2\frac{1}{2}$ for each of the centrifuges. The credit for the discovery of this process is due to G. D. Rogers of Gloucester, Mass., and its development is in the hands of R. P. Bennet of Orange, N. J.

E. SCHERUBEL

A new formaldehyde soap. FRITZ CRONER. *Seifensieder-Ztg.* 48, 3-4(1921).—The ordinary formaldehyde soaps are Na soaps which find scant usefulness. The new soft K soap is made from a mixt. of fatty and hydroxy fatty acids in such proportions that the K hydroxy fatty acid soap dissolves in the formaldehyde added, which is about 1% of the total wt. This soap is said not to be injurious to the skin and to possess great disinfecting power.

E. SCHERUBEL

Coconut-oil soaps. K. L. WEBER. *Seifensieder-Ztg.* 48, 2-3, 22-3(1921).—It is suggested that incomplete sapon. is the cause of the yellowing of coconut-oil soap. In general coconut oil soaps are cold-made and contain 12-15% of unsaponified oil; this in time changes the color of the soap on account of the decompn. products formed. Soaps containing this amt. of free coconut oil are satisfactory soaps.

E. SCHERUBEL

Determination of coconut oil in soaps by means of Polenske's method. II. R. JUNGKUNZ. Basel. *Seifensieder-Ztg.* 47, 927-9, 947-51(1920); cf. C. A. 14, 1904. —A detailed description is given with numerous literature references of the development of a method in which the Polenske No. is made the basis for detg. coconut oil (together with any palm-kernel oil) in soaps. Det. the percentage of total fatty acids in the soap, calc. the amt. of soap (7-10 g.) corresponding to 4.75 g. fatty acids, and weigh into a 300-cc. flask containing 20 g. glycerol and 1 cc. of 50% NaOH. Boil over a low flame with const. shaking to complete sapon. and to drive off nearly all H₂O (10 min.); foaming ceases when most of the H₂O is driven off. Cool to 80-90°, add 90 cc. distd. H₂O, 50 cc. dil. H₂SO₄ and 0.6 g. pumice, and finish distn. exactly as in the original Polenske method. Calc. the % coconut oil from the found Polenske No. with the aid of Arnold's table for coconut oil (C. A. 14, 1904). No distinction between coconut oil and palm-kernel oil is possible on account of the varying ratio of P.No.:R.M.No. with age of oil and kind of other fats used. With soaps containing much inorg. filler it may be necessary to sep. the filler by alc. and to evap. the alc. soap soln.

P. ESCHER

Use of tetralin in the manufacture of shoe-creams and floor waxes. I. SCHOÖN. *Seifensieder-Ztg.* 47, 937-8(1920).—The two types of shoe creams in use are (1) soaps or soap-forming substances emulsified with H₂O to a paste; (2) oils and waxes dissolved in turpentine and allowed to solidify to a paste in the container. Both types will mix with tetralin; the quality of the aq. type is improved by addition of 10-20% tetralin; 3 recipes are given as examples. The turpentine type will stand addition of 20-30% tetralin, giving better results than the usual turpentine substitutes of gasoline or naphtha; pure turpentine creams may have 10-15% tetralin incorporated without loss in quality; 4 recipes are mentioned. Floor waxes can be made with tetralin as solvent, but in such case beeswax, carnauba wax or refined montan wax (from brown coal distn.) must be added to obtain proper emulsification; 10 recipes for floor-waxes are given.

P. ESCHER

Preparation of active hydrogenation metals (BROCHET) 13. Use of hydrogenated oil in the textile industry (DARLING) 25. Preparation of active hydrogenation metals within the liquid to be treated (BROCHET) 13.

Detergent. C. M. DENNIS. U. S. 1,365,464. Jan. 11. A cleansing material adapted for general use on metals or other materials is formed of polymerization products of coal-tar naphtha mixed with other detergent or disinfecting substances, e. g., soap and H₂O.

28—SUGAR, STARCH AND GUMS

P. W. ZERBAN

Sugar-cane juice clarification for sirup manufacture. J. K. DALE AND C. S. HUNSON. Bur. Chem., U. S. Dept. Agr., *Bull.* 921, 1-15(1920).—Cane juice for sirup manuf. can be clarified by heating the juice to a temp. just below the b. p., intimately mixing with a small amt. of infusorial earth, and pumping this mixt. of juice and infusorial earth through a filter press. The sirup obtained by evapg. the filtrate is free from dregs and clearer than sirup clarified by the methods now in use which involve skimming or treatment with SO₂ and Ca(OH)₂. With a good quality of infusorial earth 10 lbs. to the juice from a ton of cane gave satisfactory results. Clarification of cane juice with infusorial earth followed by treatment with an active decolorizing

carbon produces a sirup very light in color and with little characteristic flavor. The possibility of producing for the sugar industry a better yield and quality of sugar by applying filtration with the aid of infusorial earth to the entire mill juice before chem. treatment is suggested.

W. H. ROSS

The influence of amino acids in the factory treatment of cane juice. H. I. WATERMAN AND J. W. L. VAN LIGTEN. Delft. *Chem. Weekblad* 17, 559-62(1920).—The inhibiting effect of amino acids on the alk. hydrolysis of sugars (C. A. 11, 1416) can be utilized in sugar refining. Leucine, glutaminic acid and asparagine in concns. of about 9.1% exert a marked protective influence on glucose in the lime purification of cane juice. Molasses from cane sugar refining contains enough amino acids to protect the glucose quite effectively in the lime treatment. It is well to dil. the molasses by passing live steam through it before use. The presence of sucrose, even in large amts., does not interfere with the action of the amino acids. In the case of beet juice, which contains much more N and much less glucose than cane juice, the question is not so important.

JULIAN F. SMITH

The unleachable portion of the beet. V. BARROŠ. *Listy Cukrovár.* 38, 345-9 (1920).—The amt. of residue remaining after leaching with warm water to complete soln. of all the sugar present in the beet varies within the narrow limits of 4.8-6.0%. Conditions under which the beets are grown and also their age are the prime factors causing variation in this figure.

JOHN M. KRNO

Sedimentation of sugar-house waste waters. FERDINAND SCHULZ. *Listy Cukrovár.* 38, 329-35, 337-43(1920).—The laws governing sedimentation of small particles in water suspension are discussed and mathematical relationships developed. (Cf. Allen, *Phil. Mag.* 50, 323, 519(1900)). From results of expts. on the muddy waste waters from sugar houses the following conclusions were drawn: The concn. of the sediment in suspension has no effect on the rapidity and course of the sedimentation. Only 80-85% of the earthy materials in suspension can be settled out without the aid of lime or other pptg. agents. The addition of 0.01% of CaO results in a more rapid and complete settling. Humus substance plus a small amt. of lime (0.003-0.005%) has a detrimental effect on the rapidity of sedimentation. (Cf. Andrlík and Staněk, *Listy Cukrovár.* 31, 245(1912-13); cf. C. A. 7, 3852.) The use of 0.01% of CaO overcomes the effect of the humus substance. Diffusion water has practically no effect on the sedimentation of the beet wash water.

JOHN M. KRNO

The working up of after-products according to Claassen's method. FRANZ F. KNOR. *Z. Zuckerind. czechoslov. Rep.* 44, 117-23(1920).—This method used in the refinery of Dobrovice during the campaigns of 1914-15, 1915-16 and 1916-17 gave satisfactory results. Analytical and factory data are given and tabulated for both beet and refinery juices.

JOHN M. KRNO

The working up of after-products by the Karlik-Czapikowski method. LINSBAUER ALŠ. *Listy Cukrovár.* 38, 297-301(1920).—A description of the method is given in detail. Better results are obtained with the Karlik-Czapikowski than with either the Claassen or Freitag installation.

JOHN M. KRNO

Gur-making from the juice of the date-palm (*Phoenix sylvestris*) in the Thana District of the Bombay Presidency. V. G. PATWARDHAM. *Agr. J. India* 15, 525-32 (1920).—Expts. were made to det. the best juice suitable for gur making and to get gur of solid cryst. consistency. Juice treated with formalin gave solid gur of good grain, while CHCl_3 gave solid gur, but with no grain. Juice treated with AcOH produced gur which was soft and sticky, of good light color but not of good taste. Tartaric acid added to juice gave a solid cryst. gur, with no change in color. The data

show the effect of different processes and varying amts. of acids on the qualities of gur.

J. J. SKINNER

Utilization of *Sorghum halepense* (PANTANELLI) 12. The industrial preparation of alkali cyanides from the dry distillation of viasse (SCHÖNFELD) 18.

Annuaire Sucrier 1920-1921. Liste générale des fabriques de sucre, raffineries et distilleries de France et des colonies françaises, etc. Paris: Journal des Fabricants de Sucre, rue de Richelieu 3. For review see *Centr. Zuckerind.* 29, 388(1921); cf. C. A. 14, 863.

29—LEATHER AND GLUE

ALLEN ROGERS

Some notes on the filling, polishing and varnishing of leather. ANON. *Leather Trades Rev.* 1920, 122-4, 167, 229-30.—The numerous materials used in the dressing and more particularly in the finishing of leather are grouped as follows: fatting and softening agents; perfume and scenting materials; polishing agents and assistants; materials for preserving polishes and increasing their shine; weighting and filling agents; preservatives destined for the protection and embellishment of finished leather articles. Many working formulas and methods of application are described somewhat in detail for each class of materials.

R. W. F.

The mangrove of lower Congo. R. LEMAITRE. *Bull. agr. du Congo Belge* 10, 84-9(1919).—Analyses of the bark from various heights above the root gave from 9.56 to 19.30% tannin on the dry bark. The % moisture in the bark after 15 days drying in the shade ranged from 26.6 to 46.5%. Exts. were made and analyzed with the following results:

Bark of	% tannin in total ext.	Ratio of tannin to non-tannin.	% tannin in the original dry matter.
Trunk.....	56.4	1.3	15.80
Boughs.....	44.8	0.8	15.26
Branches.....	43.0	0.7	11.61
Roots.....	50.1	1.0	10.27
Leaves.....	32.4	0.4	6.61

ALBERT R. MERZ

Note on some tanning materials of the Belgian Congo. Possibility of their utilization in the manufacture of dry extracts. ED. NIHOUL. *Bull. agr. du Congo Belge* 10, 80-92(1919).—Results of analyses of various materials were:

	% tannin in total ext.	Ratio of tannin to non-tannin.	% tannin in the original dry matter.
<i>Terminalia catappa</i>	82.75	5.0	28.3
Boembe.....	79.67	3.6	12.2
<i>Albizia Lebbeck</i>	78.59	3.6	12.5
Bempanza.....	77.53	3.4	14.6
Bakalaka-Carapa procera.....	73.81	2.8	13.4
Ikingereke.....	70.66	2.4	15.8
Wenge.....	69.24	2.2	12.0
Sowoolo or Isasange.....	67.51	2.0	14.1

ALBERT R. MERZ

Tannin-containing substances of the Belgian Congo. M. G. BATZ. *Bull. agr. du Congo Belge* 10, 93-7(1919).—*Terminalia superba*. Eng. analyzes:

	Bark.	Wood.
Moisture.....	12.40	10.16
Total ext.....	21.05	3.43
Non-tannin.....	5.10	2.73
Tannin.....	15.95	0.70
Insol.....	45.50	82.92

ALBERT R. MERZ

Determination of the tanning matter in the barks gathered by M. G. Batz in the region of N'Gazi. R. LÉMAITRE. *Bull. agr. du Congo Belge* 10, 98-100(1919).—Analyses for tanning matter and reducing substances were made on 59 samples. Of these the following may be considered as tanniferous substances utilizable in the tannery:

	%.		%.
Utachakula.....	6.60	Bokombo.....	5.74
Isali.....	9.02	Osengere.....	7.95
Wewo.....	10.44	Lisongo.....	5.80
Oleko.....	5.45	Likoko.....	6.34
Angwabele.....	16.87	Bolanda.....	8.57
		Mombaie.....	5.27

ALBERT R. MERZ

Analytical results of four samples of tanning products coming from the eastern province of the Belgian Congo. L. THON. *Bull. agr. du Congo Belge* 10, 101-2(1919).

	Moisture. %.	Total astringent acid. (St. Jean's method.) %.	Astringent acids fixed by hide. %.
Bark from Korobo (Azande).....	12.11	5.42	5.02
Bark from Bengule (Azande).....	12.56	1.80	1.69
Bark from N'Gera (Azande).....	13.08	6.40	6.06
Bark from Bengule (Azande).....	10.66	6.10	5.93

Qual. reactions with Stiasny's formaldehyde test, Br water, HNO_3 , ferrous ammonium sulfate, sulfates of Cu and NH_3 , Na_2SO_4 , concd. H_2SO_4 and lime water are placed in a table.

ALBERT R. MERZ

Effect of neutral salts on the basicity of chrome liquors. B. B. DHAVALÉ AND S. R. DAS. *J. Soc. Leather Trades Chem.* 4, 225-30(1920); cf. *C. A.* 14, 3336.—It is proposed to study this effect by the ordinary alkalimetric method since other workers have used only the electrometric. Only NaCl is studied in this paper. Other salts will follow. A chrome liquor was prepd. from 132 g. $\text{K}_2\text{Cr}_2\text{O}_7$ and 100 g. concd. H_2SO_4 by reduction with cane sugar, and then made up to 1 l. Cr was detd. by the Na_2O_2 method and acidity by the method of Procter and McCandlish. The basicity was 52:89.71. It was found that the end-point of the acidity titration was influenced by (1) the temp. and (2) the rate at which alkali was added. A titration at 50-47° required 28.5 cc.; 60-54°, 28.9 cc.; and 94-72°, 30.5 cc. When alkali was added by drops 31.3 cc. was required; 5 cc. at a time, 31.8 cc.; and 30 cc. at once, 32.6 cc. Dilm. had no influence. In the following expts. alkali was added by drops and the titration begun at 90°. It was found that there is a regular and marked increase of acidity with the increase in NaCl up to a max. at Cr:NaCl::1:281. Some expts. by Wilson (cf. *C. A.* 11, 2740) were repeated but the results were not corroborated. W. finds the same amt. of NaOH required with and without NaCl present. All the results are stated in 5 tables and 1 curve.

I. D. GARARD

Committee on limeyard control. III. Estimation of sulfide. J. E. PICKLES. *J. Soc. Leather Trades Chem.* 4, 132-5(1920).—A quick and accurate method for estg.

S in com. Na₂S and in lime liquors is given. *Direct method.* Place 70 cc. Cd(OAc)₂ soln. (62 g. Cd(OAc)₂ in 250 cc. glacial HOAc and 2250 cc. water) in a 300-cc. flask and add the Na₂S soln. Filter off the CdS ppt. and wash twice with water. Wash the ppt. into a flask, add 2 cc. glacial HOAc and excess N₂O I soln. Titrate with Na₂S₂O₃. *Distillation method.* For lime liquors a special train of ordinary lab. app. was set up. H₂S was freed with HCl and carried over in a stream of CO₂ into a soln. of Cd(OAc)₂. The ppt. was filtered off and the detn. finished as above. A diagram of the app. is given. The method is easy to perform, eliminates SO₂ and is shown to be accurate. IV. Caustic alkalinity of lime liquors. WILLIAM R. ATKIN AND JOHN ATKIN. *J. Soc. Leather Trades Chem.* 4, 263-43(1920); cf. *C. A.* 14, 2720.—Lime liquors contain (a) Ca(OH)₂; (b) NaOH; (c) NaHS and Ca(SH)₂; (d) NH₃ and negligible traces of amines and (e) Na and Ca salts of various decompn. products of proteins. $a + b$ represents caustic alkali. The application of the law of mass action is developed. Ratios of NH₄OH to NH₄Cl are plotted against p_H values and it is shown that at p_H 10.0 NH₄OH is 24% neutralized. By using a comparator and thymolphthalein as an indicator titrations were carried to a p_H of 10.0. This value gives $a + b + 0.24 d$. d is then detd. by the distn. method of Thompson and Suzuki (*C. A.* 12, 539). The salts present do not interfere. Sulfhydrate is not titrated at p_H 10.0. I. D. GARARD

The biologic significance of the tannic substances. Variations of tannin content in the bark of the chestnut tree (DOMINICIS, SPATARO) 11D. Some applications of the sulfonated products of seed and fish oils (SCURTI, FUBINI) 27. Separation and detection of lactic acid (HOFMANN) 7. The swelling of gelatin in acids (ATKIN) 2. Composition for making a leather substitute (U. S. pat. 1,365,891) 18. Jewelry (and glue-making material) (Brit. pat. 152,914) 18.

Glue or gelatin. F. H. TUNNELL. U. S. 1,364,904, Jan. 11. The solvent liquid employed in prep. glue or gelatin from glue or gelatin stock is heated so as to cause it to circulate over and through the material cyclicly during the extn. An app. is described.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

The new Peachey process of cold vulcanization. ALBERT HUTIN. *Rev. prod. chim.* 23, 497-8(1920).—A comparison is made of the older methods of vulcanization with the new Peachey process wherein rubber in soln. is vulcanized by the nascent S produced by the interaction of H₂S and SO₂. Inferior rubber may be used in this cheap process which also permits of the use of org. fillers and coloring pigments which would otherwise be destroyed by heat. Fillers can be used in large quantities, a fact which makes the process of particular value for the manuf. of linoleums, artificial leathers, etc.

ALAN LEIGHTON

Rubber in 1919. Report of progress in rubber chemistry in the year 1919. E. FONROBERT. Wiesbaden. *Kolloid-Z.* 27, 316-25(1920).—A review. II. I. M.

Rubber plants and rubber production. E. PICKENDEY. *Gummi-Zig.* 35, 147-8 (1920).—A general outline of the plantation rubber industry on the East Coast of Sumatra. G. S. W.

Rubber energy. WM. B. WIEGAND. *J. Ind. Eng. Chem.* 13, 118-25(1921).—Proof resilience is defined as the ft. lbs. of energy stored in a pound of the substance when it is stretched to its elastic limit. When rubber is stretched, some of the energy

is stored as the potential energy of strain, another part may be called reversible heat, and the remainder is frictional heat. On the return to its original shape, the potential energy will be returned in the form of useful work, the reversible heat will be reabsorbed, while the frictional heat will be increased by a further quantity of heat. It was noted that the first hysteresis loop was larger than the second, and the second larger than the third, but beyond this there was practically no change in size. A cyclic elongation of 300% was adopted since above this figure, concordant results were difficult to obtain. Since the third and succeeding hysteresis loops show practically no change in shape, each test piece was stretched twice before generating the hysteresis loops. Under these conditions, the rate of cure was shown to have some effect, being less as the length of cure increased. The addition of active pigments increased the hysteresis loss in a linear relationship. The fabric energy loss was studied by attaching one end of a 1-in. carcass section to a rigid clamp, and the other end to a pendulum, and noting the time required for the amplitude to fall from one fixed point to a second. The equation for the curve for a varying number of plies of fabric was found to be $TP = K_1 \times K_2^N$, where TP is the total period, K_1 and K_2 are empirical consts. and N is the number of plies. Over and under cure had practically no effect on TP ; the entire tread and breaker had the effect of only one ply of fabric; cord fabric was found to be about three times as efficient as square fabric in transmitting energy. Also in *Can. Chem. Met. Eng.* **5**, 42-8(1921). J. B. T.

Notes on rubber analysis. A. R. PEARSON. *Analyst* **45**, 405-9(1920).—(1) *Determination of total sulfur.* Place 20 cc. fuming HNO_3 (sp. gr. 1.5) in a 150-cc. wide-necked flask, and drop 0.500 g. finely ground rubber into the acid, bit by bit. Cover the flask with a small funnel and heat, slowly at first and then at full heat for 30 min. on a water bath. Remove the org. matter by adding solid KMnO_4 in small amts. until some of the MnO_2 remains after one hour's heating. Add 20 cc. concd. HCl and heat; when action has ceased, evap. to dryness in a porcelain dish; again add HCl and evap. to dryness. Take up in dil. HCl , filter, and det. S in the filtrate. Remove occluded Mn by boiling the ppt. for a short time with dil. HCl . Duplicate samples should check within 0.05 if proper precautions are taken in sampling. (2) *Determination of carbonates in rubber mixings.* Ca and Mg are the most frequently used carbonates. Introduce into a flask 1 g. of finely cut sample and 25 cc. glacial AcOH . Pass a current of CO_2 -free air through the app., and then heat the flask until it simmers. The gases pass through first a U-tube containing solid neutral $\text{Pb}(\text{AcO})_2$ to remove H_2S ; then a U-tube containing fused and powdered AcONa in one arm, and CaCl_2 in the other; and then through two U-tubes containing soda-lime and CaCl_2 . The detn. requires $1\frac{1}{2}$ hrs. (3) *Determination of sulfides.* The principal sulfides found are Zn and Sb, while PbS may be found in mixings containing litharge. Use an app. similar to that used for the detn. of CO_2 . Add the sample and pass N through the app. until all air is removed. Add 15 cc. AcOH , 5 cc. concd. HCl and 5 cc. water. The first U-tube contains soda-lime and CaCl_2 ; the second is a weighed U-tube $\frac{2}{3}$ filled with CuSO_4 crystals dried at 105° and the other third with CaCl_2 . N is preferable to CO_2 , as AcONa and CaCl_2 are always slightly basic, absorbing H_2S and liberating CO_2 . No S combined with rubber is eliminated by this method, only the S corresponding to Sb_2S_3 . J. B. T.

The action of concentrated sulfuric acid on natural and artificial rubber. F. KIRSCHNER, Wimpassing, Austria. *Kolloid-Z.* **27**, 311-15(1920).—Concd. H_2SO_4 on crude gum, on synthetic and vulcanized caoutchouc and on benzene solns. of these gives a product which has lost all resemblance to rubber in phys. properties, shows half as great a Br number, and is, therefore, due to an oxidation and the destruction of half of the double bonds. Efforts to regenerate rubber from this product by alcoholic KOH or aniline were unsuccessful. H. I. MATTILL

Reactions of accelerators during vulcanization. II. A theory of accelerators based on the formation of polysulfides during vulcanization. WINFIELD SCOTT AND C. W. BEDFORD. *J. Ind. Eng. Chem.* **13**, 125-8(1921); cf. *C. A.* **14**, 866.—It is thought that the acceleration of vulcanization of rubber by the action of amines, depends largely upon the action of H_2S forming polysulfides, the S of which is readily available for vulcanization. Two classes are noted: (a) H_2S polysulfide accelerators similar to yellow NH_4 sulfide; (b) carbosulphydryl polysulfide accelerators, containing the group $\dots C.SH$; including the thioureas, dithiocarbamates, etc. In class a the S is related to the sulphydryl group attached to N and in class b to C. Phenylated guanidines belong to both classes. S reacts with rubber resins and protein at 140° to form H_2S ; this, in the presence of basic accelerators forms polysulfides. These impart their S to the rubber, producing vulcanization. CaO and MgO do not function well in desiccated rubbers in which the H_2S -producing substances have been largely removed, whereas alkali and alk.-earth sulfides and polysulfides function in desiccated and synthetic rubbers. The products from hexamethylenetetramine during the cure include NH_4 and CS_2 which produce dithiocarbamates, and H_2S which with the NH_3 forms NH_4 polysulfides. Aldehyde ammonia belongs to class a. The unexpected activity of *p*-phenylenediamine is attributed to the formation of NH_3 and H_2S , together with weaker bases. Hexamethylenetetramine, aldehyde ammonia and *p*-phenylenediamine are not dependent upon the rubber resins or proteins for their supply of H_2S , the latter being one of the decompn. products. Inorg. accelerators are divided into three classes: (1) Secondary accelerators which act to form only the corresponding sulfides by decompn. of the polysulfides with the liberation of colloidal S; (2) primary accelerators which form inorg. polysulfides; (3) those accelerators which act in both capacities. PbO and ZnO are types of class 1; the alkali and alk.-earth sulfides and hydrosulfides are types of class 2; while $NaOH$, $Ca(OH)_2$, MgO and basic $MgCO_3$ are types of class 3. Class 1, or the so-called secondary accelerators, do not act as true catalysts, for once formed into sulfides, they do not again react with H_2S .

J. B. T.

The action of certain organic accelerators in the vulcanization of rubber. III. G. D. KRATZ, A. H. FLOWER AND B. J. SHAPIRO. *J. Ind. Eng. Chem.* **13**, 128-31 (1921); cf. *C. A.* **14**, 1907, 3822; **15**, 451.—In rubber-S mixts. the accelerating effect of aniline is greater than that of diphenylthiourea, judged by either the S coeff. or the physical properties. When ZnO is present, the reverse is true. ZnO either assists in the decompn. of the diphenylthiourea or combines with the decompn. products to form Zn salt, which is largely responsible for the increase both in the S coeff. and tensile strengths. Aniline does not form such a salt. In mixts. containing aniline, ZnO produces no change in the max. strength, but reduces the S coeff. ZnO increases the tensile strength in the early stages of vulcanization, and effects the same max. tensile strength at the same S coeff. with the use of either aniline or diphenylthiourea, the difference being in the shorter time required for the latter. No relation between the physical properties and the S coeff. was found.

J. B. T.

Uniformity in rate of cure of crepe from "slab" rubber. H. P. STREVENS. *Bull. Rubber Growers' Assoc.* **3**, 47-9(1921).—Crêpe prepared from "slab" rubber is found to be more variable than ordinary crêpe in rate of cure. On 11 occasions 4 samples were prepared consisting of (a) crêpe from undiluted latex; (b) crêpe from latex diluted to a standard rubber-content; (c) slab from undiluted latex; (d) slab from standardized latex. (Results for samples prepared on 7 of these occasions have been reported, *C. A.* **14**, 3169.) The av. percentage variation in time of cure found in each group of 11 samples was: (a) 4.5; (b) 4.8; (c) 20.2; (d) 16.9. (For methods of testing, cf. *C. A.* **14**, 3168.) The advantages and disadvantages of slab rubber to the rubber manufacturer are discussed.

G. S. WHITBY

Rubber preparation and the removal of lime from lime-containing water. J. C. HARTJENS. *Arch. Rubbercult.* 4, 397-428(1920).—In accord with the earlier observation (C. A. 13, 518) that, on certain estates, where the only available water shows a high content of Ca salts, diln. of the latex with water leads to premature coagulation it is now found that the removal of $\text{Ca}(\text{HCO}_3)_2$ from the water by treatment with CaO , avoids premature coagulation.
G. S. W.

The dryness of plantation rubber. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 3, 43-7(1921).—The period of mastication required to reduce each of 5 samples of rubber to the same degree of plasticity was found to show a general parallelism with the viscosity. The extreme samples were a vacuum-dried crêpe which broke down easily (9 mins.) and showed a relative viscosity of 4.16 in a 0.25% xylene soln. and a crêpe which was particularly difficult to break down (14 mins.) and showed a relative viscosity of 5.02.
G. S. W.

Application of electric power to the rubber industry. WM. E. DATE, *et al.* *J. Am. Inst. Elec. Eng.* 40, 35-47(1921).—A detailed account of the process of manuf. of the crude gum into finished rubber products with many suggestions for the installation of modern machinery.
C. G. F.

